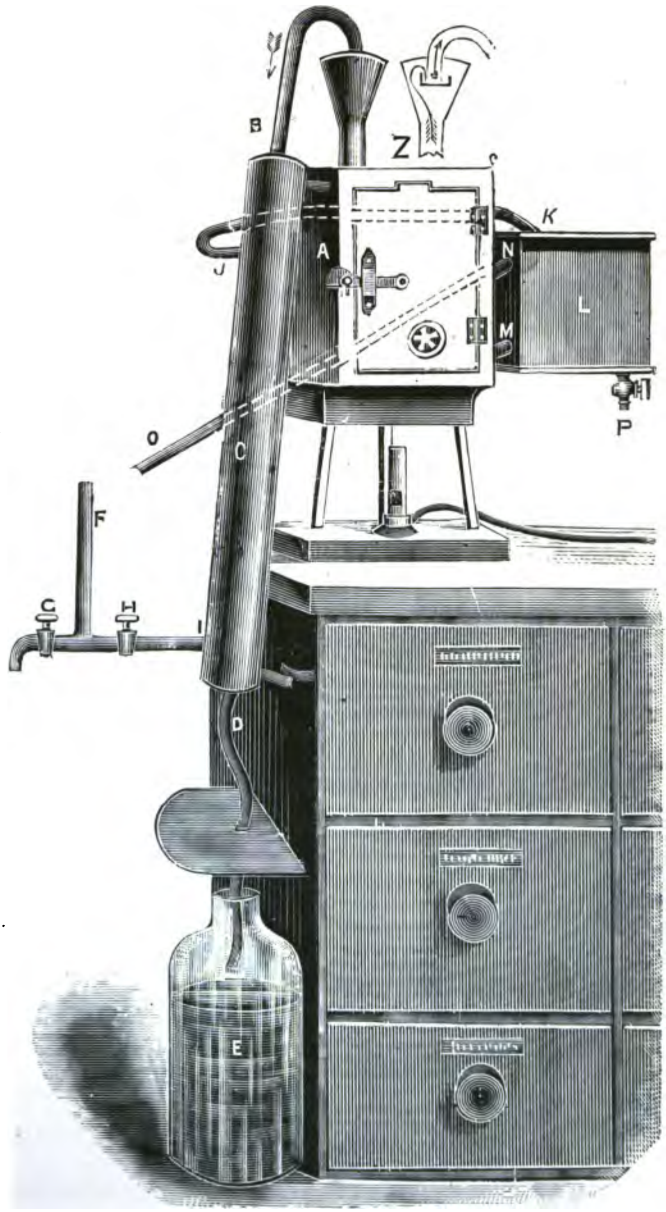

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THE ASSAY AND ANALYSIS

OF

IRON AND STEEL,

IRON ORES AND FUEL,

BY

THOMAS BAYLEY,

Associate of the Royal College of Science, Ireland.
Consulting Chemist, Analyst and Assayer, Birmingham.

AUTHOR OF

"A POCKET BOOK FOR CHEMISTS."

Reprinted from "The Mechanical World," with Additions.

ILLUSTRATED WITH

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PREFACE.

A SERIES of articles which appeared in "*The Mechanical World*" on "The Analysis of Iron and Steel," having proved useful to many practical men who, possessing some knowledge of chemistry, were enabled by their aid to make examinations of the products passing through their hands, it was represented to me that the republication of the matter in a more permanent form would widely increase its usefulness.

Having proved the value of the suggestion in the case of students of the same kind in my own laboratory, I added a few pages for the sake of completeness, and the result is this little work.

I hope it will prove useful to those for whom it is primarily intended, and to students of practical chemistry in general. Concerning the methods printed in the larger type I write from personal experience. The notes in smaller type refer to methods which I have not tested practically or which appear to me to be of minor importance, or of doubtful value, but of recent publication. The methods thus printed must stand or fall by their own merits, and to assist the reader's judgment, as far as possible I have attached the author's name to each.

I reprint Mr. F. W. Clarke's Table of the Atomic Weights, containing the result of his re-calculations, because no book on practical chemistry is complete without such a table. For ordinary purposes, however, it is unnecessary to use more than the nearest first decimal place.

7 Broad Street Corner, Birmingham,
September, 1884.

A TABLE

OF THE

ATOMIC WEIGHTS,

AS RECALCULATED BY F. W. CLARKE.

	H = 1			O = 16	REMARKS.
Aluminium	27·009	±	0·003	27·075	
Antimony	119·955	,,	0·036	120·231	Cooke's and Schneider's data.
Arsenic	74·918	,,	0·016	75·090	
Barium	136·763	,,	0·031	137·007	
Bismuth	207·523	,,	0·082	208·001	From Schneider's data.
Boron	10·941	,,	0·023	10·966	
Bromine	79·768	,,	0·019	79·951	
Cadmium	111·835	,,	0·024	112·092	
Caesium	132·583	,,	0·024	132·918	
Calcium	39·990	,,	0·010	40·082	
Carbon	11·9736	,,	0·0028	12·0011	
Cerium	140·424	,,	0·017	140·747	Buehrig's data give 141·523, O = 16.
Chlorine	35·370	,,	0·014	35·451	
Chromium	52·009	,,	0·025	52·129	From Siewert's data.
Cobalt	58·887	,,	0·008	59·023	
Columbium or Niobium	93·812		—	94·027	From one ratio only.
Copper	63·173	,,	0·011	63·318	
Didymium	142·121		—	142·502	
Erbium	165·891		—	166·273	From Cleve's data only.
Fluorine	18·984	,,	0·0065	19·027	
Gallium	68·854		—	68·963	Imperfectly determined
Glucinum	9·085	,,	0·0055	9·106	Nilson and Petterson's data.
Gold	196·155	,,	0·095	196·606	Imperfectly determined
Hydrogen	1·000		—	1·0023	
Indium	113·398	,,	0·047	113·659	Imperfectly determined
Iodine	126·557	,,	0·022	126·848	
Iridium	192·651	,,	0·033	193·094	Seubert's data.
Iron	55·913	,,	0·012	56·042	
Lanthanum	138·019	,,	0·025	138·336	
Lead	206·471	,,	0·021	206·946	

	H = 1			O = 16	REMARKS.
Lithium	7·0073	±	0·007	7·0235	
Magnesium	23·959	,,	0·005	24·014	Marchand and Sheer-er's data.
Manganese	54·855	,,	0·016	54·981	
Mercury	199·712	,,	0·042	200·171	
Molybdenum	95·527	,,	0·051	95·747	
Nickel	57·928	,,	0·022	58·062	Schneider, Sommaruga and Lee.
Nitrogen	14·021	,,	0·0035	14·029	
Osmium	198·494		—	198·951	Very doubtful.
Oxygen	15·9633	,,	0·0035	16·000	
Palladium	105·737		—	105·981	Badly determined.
Phosphorus	30·958	,,	0·007	31·029	
Platinum	194·415	,,	0·049	194·867	Seubert's data.
Potassium	39·019	,,	0·012	39·109	
Rhodium	104·055		—	104·285	Badly determined.
Rubidium	85·251	,,	0·018	85·529	
Ruthenium	104·217		—	104·457	Badly determined.
Samarium	149·801		—	150·145	
Scandium	43·980	,,	0·015	44·081	
Selenium	78·797	,,	0·011	78·978	
Silicon	28·195	,,	0·066	28·260	Very badly determined
Silver	107·675	,,	0·0096	107·923	
Sodium	22·998	,,	0·011	23·051	
Strontium	87·374	,,	0·032	87·575	
Sulphur	31·984	,,	0·012	32·058	
Tantalum	182·144	,,	0·166	182·562	
Tellurium	127·960	,,	0·034	128·254	Imperfectly determined
Thallium	203·715	,,	0·0365	204·183	Crookes's data.
Thorium	232·020	,,	0·032	232·554	
Tin	117·698	,,	0·040	117·968	
Titanium	47·980	,,	0·032	48·100	
Tungsten	183·610	,,	0·032	184·032	
Uranium	238·482	,,	0·082	239·030	
Vanadium	51·256	,,	0·024	51·373	
Ytterbium	172·761	,,	0·038	173·158	If $SO_3 = 80$, Yb = 173·016
Yttrium	88·900	,,	0·027	89·104	
Zinc	64·9045	,,	0·019	65·054	Axel Erdmann's data.
Zirconium	89·367	,,	0·037	89·375	Doubtful.

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The Analysis of Iron, Steel, Ferromanganese, etc.

The Analysis of Iron Ores and Slags.

LIST OF ILLUSTRATIONS.

ANALYSIS OF IRON AND STEEL.

CHAPTER I.

THE PREPARATION OF REAGENTS.

For ordinary purposes it is usual to determine the following substances in a sample of iron or steel: Carbon, silicon, sulphur, phosphorus, and manganese. The iron is taken by difference; the sum of the above impurities being subtracted from 100, and the difference assumed to be iron. The quantity of iron is not required to be known with great accuracy, and this method is sufficient.

The analysis of iron and steel demands the use of specially pure chemicals, and as those bought in the shops cannot be relied upon, even if sold as pure, the analyst finds it necessary to purify his chemicals by special treatment. This chapter treats of the preparation of these pure chemicals, which is the invariable prelude to the performance of the actual analysis.

Distilled Water.—In a chemical laboratory a plentiful supply of good distilled water is one of the first requisites. Distilled water can be obtained at the dealers in chemicals at about 6d. per gallon, which is not very much below the price of common sulphuric acid, but sometimes, even at this price, it is not safe to trust to its purity. If, for instance, a chemist has to determine the sulphur in a sample of steel, in which there is, perhaps, ·01 per cent. present, he must evidently be careful lest the reagents and the distilled water he uses should contain traces of sulphuric acid, so that sometimes it is almost necessary, and at all times cheaper, to make the distilled water in the laboratory, and the water oven may then be made to perform a double function. A water oven is a copper vessel with double walls. The space between the walls is

filled with water. This is kept boiling, and the temperature inside the oven thereby maintained at somewhere just below 100°C. Very often the steam from the boiling water is allowed to escape into the atmosphere, and occasionally, perhaps, the bath is neglected and allowed to boil dry, when, of course, serious consequences happen. By the arrangement shown in the illustration (frontispiece) the steam from the oven is condensed into distilled water and collected for use in the laboratory, and the possibility of accident through neglect is minimised. A is a copper water oven in the outer case of which the water boils, the steam being conducted by the pipe B to the vertical copper condenser C. The distilled water produced passes through D and is collected in the vessel E. The tube BD should be ½in. in internal diameter, must be made of block tin, and the joint between it and the oven should be made with tin and not with common solder. The tube at its lower extremity, just above the mouth of the collecting vessel, passes through a plate of tin or copper, which prevents dust falling into the distilled water, and also diverts any common water that might drip from the condenser in case of leakage. F represents the pipe supplying the ordinary service of water, and G is the tap always fixed over the sink of the laboratory. H is a smaller tap commanding the tube HI, which supplies the outer chamber of the condenser. When H is opened a stream of cold water enters the condenser at I, and, passing upwards, cools the inner tube, emerging finally at J, considerably heated. It then passes by the tube JK into the cistern L. The latter has two pipes connected to it. One of them, M, passes into the lower part of the outer case of the water oven, which is thus supplied continuously with water, already warmed, as fast as its contents boil away. The water always flows into the cistern faster than is required to supply the bath, and therefore an overflow pipe NO is provided, which delivers the excess into the sink. The cistern should be furnished with a tap, P, by means of which hot water may at any time be drawn for use if required. The amount of distilled water collected depends upon the size of the flame. A good Bunsen burner must be used, and the flame should not be large enough to pass upwards round the sides of the oven. There is always a constant stream of water

running through H, and passing away at O, where it should be distinctly warm. Only a very thin stream is required. If too much be used the supply in the cistern is kept cold, and the advantage of supplying the oven with warm water is lost. There is no necessity to have a still head on the top of the water oven; but certain precautions should be taken to prevent splashing and the mechanical carriage of water by the current of steam. The arrangement which has been found to answer best is shown at Z in frontispiece. The arrows show the course of the steam. The water in the outer chamber of the oven is, of course, maintained at the level of the escape pipe of the cistern. By the arrangement described, distilled water of excellent quality is obtained to the extent of some gallons per day. If a careless attendant lights the burner without turning on the water the bath is in danger; but it would not be difficult to arrange a tap commanding at the same time the gas and water supply, opening and shutting them simultaneously. Sometimes the supply from the main is stopped; but even then the reserve in the cistern L suffices to supply the bath for a long time. As soon, however, as the condenser gets warm at its lower end, the steam is no longer condensed, but escapes from D. The distilled water must be free from every trace of sulphur, and must be tested before use by adding one drop of hydrochloric acid, and about a cubic centimetre of barium chloride solution to half a pint of the water, after this has been concentrated to a small bulk on the water-bath. If no precipitate forms after the lapse of twenty-four hours the water is free from sulphates.

Hydrochloric Acid.—This may be bought "pure," but this does not always imply perfect freedom from sulphuric acid, and the acid should invariably be tested. It is safer to make it, and this is the cheaper plan if constant work is to be done with it. The accompanying apparatus can be used, and must vary in size according to the quantity prepared each time. A is a flask (Fig. 1) into which is placed the usual mixture of salt, sulphuric acid, and a little water. The best proportions are salt 6lb., sulphuric acid 110 fluid ounces, water 60 fluid ounces. The sulphuric acid should be free from arsenic. Common acid made from brimstone will do, if it has been previously tested for this

impurity and found to be free from it. The acid and water should be cautiously mixed in an earthenware vessel, and allowed to become quite cold before use. The salt should be cut into pieces as large as a walnut, and the liquid poured upon it down the funnel. At first no heat need be applied, but after the action has slackened the flask must be gently heated by the Bunsen burner beneath the sand-bath D. The hydrochloric acid gas passes into B, which is a Woulffe's bottle, containing a little water. As soon as the water in B is saturated with acid, the gas passes over into C, and saturates the pure distilled water placed in that

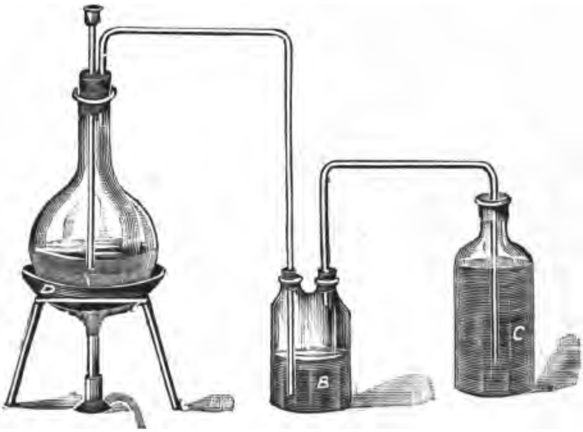

FIG. 1.

receptacle. C should not be placed in position until the analyst has tested the gas coming over, and found it to contain no free chlorine. This is done by causing it to pass for a few minutes into distilled water, and adding a solution of potassium iodide and starch to the liquid so obtained. If chlorine is present a blue colour at once appears. While the hydrochloric acid is contaminated with chlorine it may be condensed in water, but this solution must be kept separate, and used for the common purposes of the laboratory. The pure solution must be allowed to remain exposed to the gas until it has a greater density than 1·1, and must then be removed, allowed to cool, and diluted to

this gravity with pure distilled water. Of course, as long as gas comes over water must be placed to condense it. The acid in B is fit only for rough purposes, as for cleaning apparatus.

NITRIC ACID.—This acid, when used for the analysis of steel and iron, must be quite free from chlorine and sulphuric acid. It is easy to obtain it in this condition. Enough of the pure acid of the shops to half fill the body of the retort (Fig. 2) is taken, and the beak of the retort is placed within the neck of a bottle, which being used to store the acid is well stoppered and capped. A small flame is placed under the retort, but this must not be large enough to cause the contents to boil. About 5 cubic centimetres of a strong

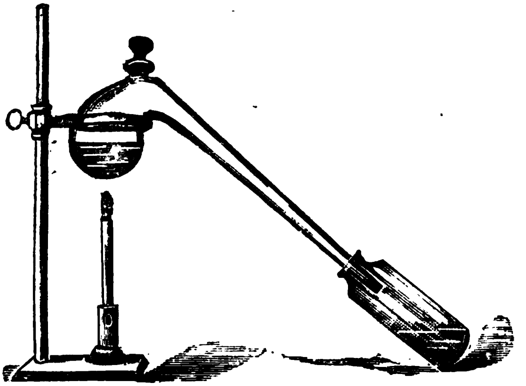

FIG. 2.

solution of barium nitrate, and about the same quantity of strong silver nitrate solution, should be added to the nitric acid. The silver salt serves to keep chlorine, and the barium salt to keep sulphuric acid, from distilling over. Although the acid is not allowed to boil, vapour rises from its surface, and drops of distilled nitric acid slowly trickle into the bottle. The flame need only be as large as an ordinary candle flame. After some hours, a quantity of pure nitric acid will have passed over, and this must be carefully preserved in the bottle. For ordinary use it must be diluted with distilled water until the gravity of the mixture is 1·2.

CHAPTER II.

THE DETERMINATION OF MANGANESE.

In order to determine manganese in iron or steel the sample is first brought into solution, the iron precipitated and filtered off, and the manganese then estimated in the filtrate. The first step is to weigh out accurately two grammes of the sample, which should consist of borings made with a tool free from grease. This quantity must be transferred, without loss, to a tall beaker, of about 40 ounces capacity, and well covered with pure hydrochloric acid. The beaker, having been covered with a clock glass, is placed upon a sand bath or hot plate and allowed to stand until the iron has dissolved. Nitric acid is now added to the solution, which at first becomes dark coloured, owing to the generation of nitric oxide, which forms an unstable compound of dark colour with proto-salts of iron. After the addition of some more nitric acid the whole of the iron is brought into the ferric condition, and the nitric oxide is given off with effervescence, leaving the solution yellow. The solution is evaporated down to dryness, heated strongly on a hot plate to destroy organic matter, and the residue afterwards dissolved in hydrochloric acid and a few drops of nitric acid. The beaker is next about two-thirds filled with water, and the contents raised to the boiling temperature. As soon as this point is reached the clock glass is removed, and ammonia solution very cautiously added, and at the same time the liquid is briskly stirred with a glass rod. The solution, at first faintly yellow, soon begins to appear darker, and when this point is reached, ammonia, purposely made very dilute, is added with caution, a little at a time, and the stirring continued. The liquid, which is by these means finally made of a full mahogany colour, must remain quite clear, and no trace of permanent precipitate should be formed. About a couple of ounces of ammonium acetate solution, which has been raised to boiling in a small beaker, are now mixed with the solution of the iron. The result is an immediate precipitation of basic acetate of iron, which

insoluble under the conditions of the experiment. The precipitate should be brick red; if it be dark red, enough ammonium acetate has not been used, and more must be added. The mixture should now be boiled, but only for a few minutes, to make the precipitate granular. If the boiling is too long continued the precipitate becomes slimy, and afterwards clogs the filter. The hot solution is covered with a glass plate, and allowed to stand until the precipitate has subsided, and then filtered while still hot through a large corrugated filter into a flask of half a gallon capacity. If everything has gone well the filtrate is perfectly clear and runs through the filter almost as fast as it can be poured on. The paper containing the red precipitate is now transferred to the beaker, which need not be washed free from the last traces of precipitate, and enough dilute hydrochloric acid added to redissolve the iron. The solution so obtained is diluted to the same bulk as before, and the precipitation with ammonium acetate repeated. The filtrate is mixed with the first. This second precipitation is necessary, especially in the analysis of ferromanganese or spiegeleisen, because some of the manganese is almost invariably carried down with the iron in the first instance. The red precipitate must be tested for manganese by Crum's method. A portion of it is removed to a test tube and boiled with peroxide of lead and nitric acid of density 1·2. The peroxide of lead is heavy, and settles readily, and the clear liquid is pink—if even a trace of manganese is present. After two precipitations of the iron no manganese should be found in the red precipitate. If a permanent precipitate is formed during the addition of ammonia in the first instance, manganese will almost certainly be found in the first batch of red precipitate. The bulky solution containing the manganese must now be allowed to cool. The cooling may, of course, be hastened by causing a stream of cold water to play over the outside of the flask. In the analysis of iron or steel, where the amount of manganese is usually small, the filtrate from the red precipitate may be considerably concentrated before the next operation. Any red precipitate produced during the ebullition must be filtered off. When the solution is quite cold, bromine is added in sufficient quantity to make it dark brown. The bromine is added in

several instalments, and the flask shaken at each addition. To the brominated liquid strong ammonia is boldly added in sufficient quantity to make the liquid alkaline, and the flask is then shaken. The manganese is almost immediately separated as black peroxide, which if present only in small quantity, at first causes merely a brown coloration. The liquid is heated to boiling, and the precipitate is collected on a Swedish or Rhenish filter paper, and washed with hot water. It is then dried on the paper and burnt in a crucible, preferably of platinum. It is finally ignited as strongly as possible over a Herepath blow-pipe flame for five minutes, then cooled and weighed. The manganese is brought by these means to the condition of Mn_3O_4, and the weight of the precipitate multiplied by ·7205 gives the weight of the metallic manganese present in the 2 grammes of iron dissolved. This quantity multiplied by 50 gives the percentage. Of course the filter ash must be taken into account. Sometimes, owing to the presence of a trace of organic matter in the reagents, a small quantity of iron remains in the solution, and is precipitated and weighed with the manganese. It is therefore necessary to test the Mn_3O_4 for iron after weighing it. This is done by dissolving it in hydrochloric acid, and testing a drop of the solution with potassium ferrocyanide solution in a porcelain dish. If a blue precipitate appears, iron is present, and the remainder of the solution of manganese must be diluted in a small beaker, raised to boiling, rendered basic (dark red) by ammonia, and the iron precipitated with ammonium acetate. The red precipitate must be filtered off, well washed with hot water, dried, and ignited. The Fe_2O_3 thus obtained is deducted from the Mn_3O_4; as first weighed, and the corrected weight is the true weight of the manganese oxide.

Some chemists estimate the iron in the precipitate colorimetrically. A solution of ferric nitrate is made containing 1 gramme of iron per litre. The precipitate to be tested is dissolved in nitric acid with a drop of hydrochloric acid, the solution diluted to 50 cubic centimetres with water in a glass cylinder, a little dilute solution of potassium ferrocyanide added, and the tint compared with that produced in a similar way by varying amounts of the

standard solution of iron. The small amount of iron, about half a milligramme, in the ash of a good filter paper may be neglected.

The oxide of manganese obtained by igniting the hydrated peroxide is not strictly the trimanganic tetroxide, but is liable to slight variations in the amount of oxygen. For this reason, when the manganese in a spiegeleisen or ferromanganese is estimated, it is preferable to first weigh the manganese after ignition of the precipitate, and afterwards to convert it into sulphate of manganese and weigh again. A slight excess of pure sulphuric acid and a few crystals of pure oxalic acid are placed in the crucible, which is heated on an iron plate or sand bath, while covered with a watch glass. The oxalic acid favours the reduction of the manganese, which is converted into sulphate by the sulphuric acid. The contents of the crucible are taken down to dryness over a small gas flame, and the residual sulphate of manganese heated to very low redness. The composition of the sulphate is quite definite if the ignition has not been made at too high a temperature, and the weight of the precipitate multiplied by ·3642 gives the weight of metallic manganese. Spiegeleisen and ferromanganese frequently contain small quantities of copper, and this metal is precipitated with the manganese. Nickel and cobalt, if present in traces, would also pass to some extent into the manganese precipitate. The copper may be removed by sulphuretted hydrogen in the original acid solution, or thrown down by zinc from a dilute sulphuric acid solution of the precipitate and weighed as metal. In the latter case only a small excess of acid must be present, and the solution must be decanted from the copper as soon as the zinc is completely dissolved, otherwise the film of copper is partially redissolved by the acid. When the copper is removed by sulphuretted hydrogen in the original solution, the free acid must not be in great excess, the liquid must stand some hours, and the filtrate must be boiled to remove sulphuretted hydrogen. The iron is then oxidised with nitric acid, and precipitated as basic acetate.

The ammonia used in the determination of manganese should be pure, and the ammonium acetate made specially in the following manner: The best acetic acid should be

obtained and purified by distillation. A quantity of the purified product should then be placed in the bottom of a capacious beaker, and ammonia vapour, generated by boiling ammonia of ·880 specific gravity in a flask with a safety tube, passed into it. The action is energetic, and the contents of the beaker are agitated, hence the necessity for a beaker of considerable capacity. The acetic acid is neutralised by the ammonia and ammonium acetate is formed. If the ammonium acetate solution be alkaline at the conclusion, enough of the distilled acetic acid is added to give an acid reaction with litmus paper.

The following list of results obtained by different chemists in the determination of manganese, is given by Mr. W. Kent, of Pittsburg. The sample was very carefully prepared, so as to be of the same composition throughout.

No.	Chemist.	Manganese.	Process.
1.	A.	·434	Acetate sodium and bromine.
2.	A.	1·140	
3.	A.	·610	
4.	B.	·613	
5.	B.	·580	
6.	B.	·330	Nitric acid and chlorate of potassium.
7.	C.	·324	
8.	D.	·451	Not reported.
9.	D.	·453	
10.	E.	·303	Acetate with modifications.
11.	F.	·391	Acetate process.
12.	F.	·385	Nitric acid and chlorate of potassium.
13.	G.	·406	Acetate with modifications.
14.	G.	·408	
15.	H.	·351	Acetate ammonium and bromine.
16.	H.	·380	
17.	I.	·562	Acetate sodium and bromine.
18.	I.	·619	
19.	J.	·439	
20.	J.	·374	
21.	J.	·313	Results 19 and 20 redissolved and determined by nitric acid and chlorate.
22.	J.	·333	
23.	J.	·356	Nitric acid and chlorate of potassium direct.
24.	J.	·333	

Mr. F. H. Williams recommends, for the volumetric estimation of manganese, a method which has been adopted in the laboratory of the Vulcan Steelworks. It consists in precipitating the manganese as peroxide, dissolving the precipitate in dilute sulphuric acid in the presence of an excess of standard solution of oxalic acid,

and titrating with permanganate the oxalic acid left undecomposed. One or two grammes of the sample are weighed out and dissolved in 40 or 50 cubic centimetres of concentrated nitric acid. The solution is filtered to remove carbon and silica and the asbestos filter washed with nitric acid. Pulverised chlorate of potassium is used in a boiling solution to precipitate the manganese as peroxide. The washed precipitate is treated with excess of standard oxalic acid, diluted to 60 or 70 cubic centimetres with water, and 3 or 4 cubic centimetres of concentrated sulphuric acid added. The mixture is heated to 70 or 80°C., and titrated while hot with permanganate (1c.c. = ·00 gramme Fe).

F. Beilstein and L. Jawlin make use of the fact that iodine throws down manganese from a solution of mangano-cyanide, but produces no precipitate in a solution of ferrocyanide. They pour the solution of ferric and manganese salts into excess of a concentrated solution of potassium cyanide, and filter off a slight insoluble residue, which always remains, but contains no manganese. Iodine is then added until all the cyanide has been decomposed, and the slight excess is removed by addition of soda. The precipitated manganese oxide is filtered off, washed, dissolved, and precipitated as sulphide. About 30 grammes of iodine are required for each estimation.

Volhard has proposed the following method for the estimation of manganese: The sample is dissolved in a mixture of three volumes dilute sulphuric acid (1·13 sp. gr.) and one volume of nitric acid (1·4 sp. gr.), and the solution evaporated to dryness on the water-bath. If it is rich in carbon the residue is dissolved in hydrochloric acid and water, filtered, and the filtrate, after the addition of a little sulphuric acid, evaporated till fumes begin to come off, so that all trace of carbon compounds are destroyed. If the steel is low in carbon, the original solution, after evaporation to dryness, is gently heated, redissolved in nitric acid, and put into a measuring flask. After neutralisation with caustic, or carbonate of, soda, oxide of zinc is gradually added to precipitate the iron as hydrate. The solution after standing a short time is filtered and diluted to a known volume. An aliquot portion of the filtrate is acidified with one drop of nitric acid, and heated to 100°C. The flame is removed and permanganate run in by drops while the flask is continually agitated. As soon as the supernatant liquid shows on settling a pink colour, the flask is again heated and shaken. If the colour disappears, a few more drops of permanganate are added till a permanent slight excess is present. Too much free acid retards the action. The method depends upon the separation of iron by precipitation with zinc oxide, and the subsequent decomposition of the manganous salt by the permanganate, with formation of (hydrated) MnO_2. According to Volhard manganous oxide is absent from the precipitate in presence of a sufficient amount of zinc, magnesium, calcium, or barium salt. Volhard gives analyses which indicate that the method is accurate.

Mr. Pattinson estimates manganese volumetrically by precipitating as dioxide, dissolving the precipitate in presence of a ferrous salt, and determining the excess of the latter. It is necessary to

have a certain amount of ferric chloride or zinc chloride present during the precipitation of manganese in order to obtain the latter entirely in the form of dioxide. The reagents used are: (1) A 1·5 per cent. solution of bleaching powder, or saturated bromine water. (2) Light granular calcium carbonate obtained by precipitating $CaCl_2$ by Na_2CO_3 at 180°F. (82°C.). (3) A 1 per cent. solution of $FeSO_4$ in H_2SO_4 (1 in 4). (4) Standard potassium bichromate (1c.c. = ·001 gramme Fe). The process is as follows, as applied to manganiferous ores: 10 grains of the ore dried at 212°F. (100°C.) are dissolved in a 20oz. beaker in about 100 fluid grains of HCl (sp. gr. 1·18). $CaCO_3$ is then added until free acid is neutralised and the liquid becomes slightly reddish. Six or seven drops of HCl are now added, and 100 grains of the bleaching powder solution or 500 grains of the bromine water, and boiling water is run in until the temperature equals 140° to 160°F. (60° to 70°C.); 25 grains of $CaCO_3$. are added, and the whole well stirred. If the supernatant solution has a pink tint the permanganate is reduced by a few drops of alcohol. The precipitated oxides of iron and manganese are filtered off and washed. One thousand grains of the acidified $FeSO_4$ solution are measured into the 20oz. beater originally used, and the filter with its washed contents added. The excess of $FeSO_4$ is then determined by the bichromate solution. For the analysis of spiegeleisen, the following proportions are recommended: 10 grains of the sample are dissolved in 120 grains of HCl, and 50 grains of HNO_3 (sp.gr. 1·4) afterwards added. One thousand grains of bleaching powder solution followed by 25 grains of $CaCO_3$ are employed. For ferromanganese an amount of sample containing 2 to 4 grains of manganese is employed, and 400 grains of bleaching powder solution are required. For steel 50 grains of the sample are employed and dissolved in 350 grains of HCl, followed by 90 grains of HNO_3.

Colorimetric methods for the estimation of manganese, depending upon oxidation to permanganate, have been several times proposed. According to one method one-tenth of a gramme of the sample is dissolved in nitric acid and the solution is boiled with peroxide of lead and subsequently diluted. The intensity of the tint is compared with the tint of solutions of standard permanganate. According to other methods the oxidation of the manganese is effected by fusion with sodium carbonate and nitre.

CHAPTER III.

THE DETERMINATION OF PHOSPHORUS.

A fairly accurate method of estimating phosphorus in steel or iron is by precipitation as ammonium magnesium phosphate. Take 5, or better 10, grammes of the sample and dissolve in a mixture of hydrochloric and nitric acids. Every 5 grammes should have 40 cubic centimetres of hydrochloric acid (sp. gr. 1·1) and 30 cubic centimetres of nitric acid (sp. gr. 1·4). If the sample is in the form of borings it is best to place the acid in a large wide beaker and gently heat it, and then add the steel a little at a time to prevent the action becoming too violent. After complete solution has been effected the contents of the beaker are diluted, without filtration, to a considerable volume with water, and sufficient sodium sulphite added to reduce the whole, or nearly the whole, of the iron to the state of proto-salt. There must, however, be enough iron left in the state of ferric salt to make the subsequent precipitate produced by ammonium acetate of a red colour, otherwise some of the phosphorus may be lost. The sulphite of sodium should be added while the solution is cool, in presence of a good excess of hydrochloric acid, and as the liquid becomes warm the reduction of the iron takes place. The boiling hot liquid is treated with ammonia, as described in the chapter on the Determination of Manganese, and acetate of ammonium is afterwards added. The greater part of the iron being in the state of proto-salt is not precipitated, but the small quantity of iron purposely left in the state of ferric salt is precipitated as basic acetate, and this precipitate contains the whole of the phosphorus. The phosphate of iron is white, but in order to guard against error it is necessary to have a slight excess of ferric iron, and this causes the precipitate to be of a pink or red colour. If the precipitate is not red a little potassium permanganate solution or bromine water should be added to the boiling liquid. The precipitate is filtered off and washed once with water. The filtrate as it runs through must be clear, but if it afterwards becomes turbid in the receptacle no notice need be taken, as this is caused by

oxidation and will not affect the analysis. The filtrate, whether clear or turbid, is thrown away. The precipitate is dissolved in hot hydrochloric acid, the liquid filtered, and half an ounce or so of citric acid dissolved in the clear solution. Strong ammonia (sp. gr. ·880) is now cautiously added until the liquid smells strongly of this reagent. The citric acid prevents the precipitation of the iron, and the liquid, after the addition of the ammonia, remains clear, but should have a green tint. The whole volume of the solution at this stage should not exceed 2 or 3 ounces. A few cubic centimetres of "magnesia mixture" are now added, and the liquid set aside to cool and occasionally briskly stirred. After a time a crystalline precipitate of ammonium magnesium phosphate makes its appearance, and this, after the lapse of twelve hours, must be filtered off and washed with ammonia water, made by mixing one volume of strong ammonia with seven volumes of distilled water. The precipitate is afterwards ignited, first over a Bunsen burner and next over a Herepath blowpipe, and weighed, and the weight multiplied by ·2793 gives the weight of phosphorus present. The amount must be calculated to percentage.

It is occasionally advisable to test the magnesium pyrophosphate for arsenic. The precipitate, after weighing, is dissolved in warm hydrochloric acid, the solution diluted with water, heated to about 70°C., and subjected to a current of sulphuretted hydrogen. A yellow precipitate indicates arsenic. In presence of this element it is advisable to treat with sulphuretted hydrogen at an earlier stage of the analysis after the solution of the basic acetate precipitate in hydrochloric acid. The yellow sulphide of arsenic is filtered off, and the filtrate freed from sulphuretted hydrogen by boiling. The phosphoric acid can then be determined in the usual way. The arsenic precipitated in this way is not the whole of the arsenic contained in the iron—a considerable portion is said to be volatilised as chloride during the evaporation to dryness of the original solution. Or the mixed precipitate of phosphate and arseniate of magnesium and ammonium can be dissolved in a little hydrochloric acid, the arsenic precipitated, at 70°C., by sulphuretted hydrogen, and the phosphate reprecipitated by adding ammonia to the filtrate.

PREPARATION OF MAGNESIA MIXTURE.—Dissolve 83 grammes of crystallised magnesium sulphate in boiling water, add 5 cubic centimetres of hydrochloric acid, and then 82 grammes of crystallised barium chloride previously dissolved in water. Filter off a few drops of the solution and add dilute sulphuric acid. If this gives a precipitate add a little more magnesium sulphate. Then decant and filter, mix the filtrate and washings, and concentrate by evaporation. When cool transfer to a litre flask, add 165 grammes of pure ammonium chloride, 260 cubic centimetres of ammonia, and then water to the mark. Allow to stand a few days and filter if necessary.

THE DETERMINATION OF PHOSPHORUS BY MOLYBDIC ACID.—Phosphorus can also be estimated in iron and steel by taking advantage of the fact that molybdic acid forms with phosphoric acid and ammonia a compound insoluble in nitric acid. This compound contains a very large percentage of molybdic acid and a small percentage of phosphoric acid, and is therefore suitable for the determination of small quantities of phosphorus, such as are found in iron and steel, because the phospho-molybdate which results even from a very small quantity of phosphorus is a comparatively large and heavy precipitate. This can be made clear by an example. Suppose 5 grammes of steel containing ·05 per cent. of phosphorus are treated for the estimation of phosphorus by the magnesia method, the precipitate will in this case, after ignition, consist of magnesium pyrophosphate, and will weigh ·009 gramme, which is rather a small quantity. If the same quantity of the steel were treated by the molybdic acid method, the precipitate would weigh ·153, which is a quantity 17 times as great as the former, and therefore proportionately less influenced by common errors of experiment, such as errors of weighing. On the other hand, the molybdic acid method seems to yield somewhat different results in the case of different analysts, probably owing to small differences in their modes of operating, or to variations in the composition of the yellow precipitate. In one case two experienced chemists analysed the same steel: the first obtained ·125 per cent. of phosphorus, and got practically the same result by several repetitions of the analysis: the second obtained ·104 per cent., and also obtained confirmatory results on repetition. The magnesia method gave ·100 per cent., which was probably a little below the truth, as the ammonium magnesium phosphate is sensibly soluble in its mother-liquor. It is a matter of opinion,

therefore, which of these two methods of estimating small quantities of phosphorus, such as exist in iron and steel, is the better. Probably for ordinary estimations the molybdic acid method is better, as being quicker; but in cases where greater accuracy is desired, even at the expense of time and trouble, it is preferable to take a larger quantity of the sample and use a combination of the two methods.

The estimation by molybdic acid is performed on 2 grammes of the sample, or even on 1 gramme in cases of high percentage. The steel or iron is added in small quantities at a time to about 50 cubic centimetres of nitric acid (sp. gr. 1·2), which dissolves the iron and oxidises the phosphorus to phosphoric acid. The solution is next evaporated to complete dryness on an iron plate or sand bath, allowed to cool, moistened with pure hydrochloric acid, and again evaporated to dryness to insure the complete separation of silicic acid, which itself forms a precipitate with molybdic acid. The dry black residue is next dissolved in nitric and hydrochloric acids, as little of the latter being used as will suffice to cause solution. The liquid is filtered and diluted, evaporated to a syrupy condition, and diluted again with nitric acid. This is repeated twice in order to drive off a portion of the hydrochloric acid. The solution becomes each time of a lighter colour, and the fact may be used as a criterion of the amount of hydrochloric acid present. The liquid, diluted sufficiently with nitric acid to cause it to flow freely, is transferred to a "precipitating glass" or "Clark's glass" of about 4 ounces capacity, and as much pure solid ammonium nitrate as it can take up is dissolved in it. Fifteen—or in cases of high percentage 30—cubic centimetres of the molybdic acid solution are now poured into the beaker in which the solution of the steel was evaporated, and then into the precipitating glass. By this means the small quantity of the steel solution left in the beaker is rinsed into the main quantity without the use of water. The precipitating glass is then placed in a vessel of water of a temperature of 40° C., and maintained at this temperature for ten hours. A heavy yellow precipitate is produced in the presence of phosphorus, and this is separated from the liquid by filtration. The filter paper must not be more than two inches in diameter, and the last traces of

precipitate must be detached by a "policeman" (a short piece of caoutchouc tubing at the end of a glass rod), and rinsed into the filter by some of the clear filtrate. The filter and contents are next washed *three times* with a solution of one part of nitric acid (sp. gr. 1·2) in nine parts of water. The apex of the filter is then perforated, and the contents washed by a fine stream of hot water into a previously weighed porcelain crucible of one ounce capacity. The flap of the filter must be turned back to make sure that no phospho-molybdate has escaped the jet of water from the wash-bottle. Two or three drops of nitric acid are added to the contents of the porcelain crucible, which is then heated over a water bath until the solution is entirely evaporated. The crucible is finally dried in the water oven and weighed. If the quantity of precipitate is considerable it may be dried on the filter and scraped off with a sharp knife. The weight of the phospho-molybdate multiplied by ·0163 gives the quantity of phosphorus contained in the steel weighed out.

PREPARATION OF MOLYBDIC SOLUTION.—25 grammes of molybdic acid (MoO_3) are dissolved in 50 cubic centimetres of ammonia (sp. gr. ·880) and 50 cubic centimetres of water; filter, pour into 375 cubic centimetres of nitric acid (1·2 sp. gr.), stir, and allow to stand some days. Decant from any precipitate of phospho-molybdic acid due to traces of phosphorus in the material.

A combination of the magnesia method and the molybdic acid method has been suggested by Mr. Arnold and others. The basic precipitate produced by ammonium acetate, which contains all the phosphoric acid, is dissolved in hydrochloric acid, evaporated to the lowest possible bulk, and precipitated with ammonia. The precipitate is dissolved in nitric acid (sp. gr. 1·4), and the molybdic acid reagent added to the boiling solution. In order to insure the precipitation of the whole of the phosphoric acid the boiling is continued until some molybdic acid also comes down. The yellow precipitate is washed with dilute nitric acid until free from iron, and then dissolved in ammonia, the liquid filtered, and the filter washed with hot water. A few drops of hydrochloric acid are added to the ammoniacal solution, and then a few cubic centimetres of magnesia mixture. The precipitate comes down in an hour or two if the liquid is occasionally stirred. The volume of the final liquid need not be more than 2 ounces. Ten grammes of the sample should be taken, and a corresponding volume of molybdic acid solution is, of course, required.

Dr. J. Lawrence Smith uses the following modified process of determining phosphorus in iron and steel: One gramme of the sample is treated with 3 or 4 cubic centimetres of water, and then with 15 cubic centimetres of aqua regia, the latter

being adding gradually. The solution is evaporated to dryness, and the residue heated to 140° to 150° C. for an hour, to render silica insoluble. The residue is then dissolved in 3 or 4 cubic centimetres of hydrochloric acid and as much water, and the solution filtered and made up to 100 cubic centimetres. From 90 to 92 cubic centimetres of this solution are treated with excess of sodium or ammonium sulphite, and the excess of sulphurous acid driven off by boiling. Ammonia is then added to the warm solution until a permanent greenish precipitate begins to appear. About 20 cubic centimetres of acetic acid are added, and 1 or 2 cubic centimetres of ammonium acetate solution. The 8 or 10 cubic centimetres of the solution not subjected to the action of sulphurous acid, and 200 or 300 cubic centimetres of water, are then added and the mixture boiled for from one half to one hour. The result is the formation of a basic salt, containing practically all the phosphorus. This precipitate is filtered off and dissolved in a hot mixture of 5 cubic centimetres of hydrochloric acid and the same volume of water. The solution is evaporated to dryness, and the residue treated with 1 or 2 cubic centimetres of nitric acid and an equal volume of water. Ammonia is added until a permanent precipitate begins to appear, which is again dissolved by a drop or two of nitric acid. The phosphoric acid is then precipitated by molybdic acid solution, 30 cubic centimetres of the reagent being used, and the digestion continued for twenty minutes at 80° C. The precipitate is washed with distilled water and dried at 120° C. and weighed.

Mr. A. E. Haswell determines the phosphorus and silicon in iron and steel by treatment with a 7 per cent. solution of double chloride of copper and ammonium at the lowest possible temperature in a closed flask. The carbon, silicon, sulphur, and phosphorus remain in association with the reduced spongy copper. This is carefully washed, dissolved in nitric acid, the silica separated and washed, and the phosphorus precipitated first with molybdic acid and subsequently with magnesia mixture. The author states that the presence of copper salts does not interfere with the precipitation of phosphorus as yellow precipitate.

Mr. E. Riley, at a meeting of the Chemical Society, in 1878, gave some results of the determination of phosphorus by different operators and by two methods. The results of the magnesia and citric acid method he considers very trustworthy, when the operator is skilled and careful. The results obtained by the molybdic acid are low. Mr. Riley proposes the following modification of the molybdic acid method: The steel is dissolved in nitric acid (sp. gr. 1·2), excess being avoided as much as possible. The solution is diluted to rather more than half a pint, sodium sulphite is added to reduce the iron, and the excess of sulphurous acid boiled off. The phosphoric acid is then thrown down combined with a small amount of peroxide of iron by ammonium acetate and acetic acid. The precipitate is dissolved in hydrochloric acid, the solution made alkaline with ammonia, and the precipitate formed dissolved in nitric acid (sp. gr. 1·4). The solution is then precipitated with molybdate of ammonia in the ordinary way.

Mr. F. E. Bachman, of the St. Louis Ore and Steel Company, Mo., has given the results of determinations by different chemists of the phosphorus contained in the same pig. The analyses are from the same lot of drillings, except 8 and 9, and 28 to 32 inclusive, which are from drillings made at an earlier period. The brackets indicate duplicate determinations. Bachman states that of three chemists working the acetic and citric acid methods two are wrong; of three who worked the direct molybdate method two are wrong; of two working the modification of the molybdate magnesia method, in which there is a large quantity of chlorides present with the nitric solution when phosphorus is precipitated, both are wrong; and of ten working the method so that there is only nitric acid and ammonic nitrate present with the iron solution, nine are within the limits of error. The experiments therefore show the necessity of eliminating hydrochloric acid as completely as possible.

No.	Chemist.	°/₀ P.	Method.
1.	... A. ...	·151 ...	
2.	... A. ...	·154 ...	Molybdate and magnesia.
3.	... B. ...	·152 ...	
4.	... B. ...	·153 ...	
5.	... C. ...	·1519...	
6.	... C. ...	·1523...	Molybdate and magnesia modified.
7.	... D. ...	·152 ...	
8.	... E. ...	·154 ...	Molybdate and magnesia.
9.	... E. ...	·156 ...	
10.	... F. ...	·146 ...	
11.	... G. ...	·141 ...	
12.	... G. ...	·145 ...	
13.	... H. ...	·143 ...	Molybdate and magnesia modified.
14.	... I. ...	·164 ...	
15.	... I. ...	·165 ...	
16.	... J. ...	·147 ...	
17.	... J. ...	·150 ...	Molybdate direct.
18.	... J. ...	·148 ...	
19.	... J. ...	·150 ...	
20.	... J. ...	·147 ...	Molybdate and magnesia modified.
21.	... J. ...	·132 ...	Molybdate direct.
22.	... J. ...	·129 ...	
23.	... K. ...	·151 ...	Acetic method.
24.	... K. ...	·152 ...	
25.	... L. ...	·1106...	
26.	... L. ...	·096 ...	
27.	... L. ...	·100 ...	Magnesia and citric acid.
28.	... L. ...	·097 ...	
29.	... M. ...	·130 ...	
30.	... N. ...	·152 ...	
31.	... N. ...	·154 ...	Molybdate and magnesia modified.
32.	... O. ...	·151 ...	
33.	... O. ...	·152 ...	
34.	... O. ...	·145 ...	Molybdate direct.

No.	Chemist.	% P.	Method.
35.	... P. ...	·151 ...	Molybdate and magnesia modified.
36.	... P. ...	·147 ...	Molybdate and magnesia modified.
37.	... P. ...	·150 ...	Molybdate and magnesia modified.
38.	... P. ...	·147 ...	Molybdate and magnesia modified.
39.	... P. ...	·109 ...	Molybdate and magnesia modified.
40.	... P. ...	·139 ...	Molybdate direct.
41.	... P. ...	·140 ...	Molybdate direct.
42.	... P. ...	·152 ...	Molybdate and magnesia modified.

On the other hand some results obtained by the author and confirmed by Mr. A. H. Allen, seem to indicate that in the absence of hydrochloric acid, or chlorides, the precipitation by molybdic acid is very imperfect or fails altogether.

Messrs. Muhlenberg and Drown use the sulphuric acid solution after the determination of silica in the estimation of phosphorus. The sample is dissolved in nitric acid, the solution evaporated with excess of sulphuric acid and then diluted, boiled and filtered to separate silica. The sulphuric acid is afterwards expelled by ignition, and the dry residue taken up with nitric acid; the phosphorus is precipitated by molybdate, the yellow precipitate redissolved, and the phosphorus weighed as magnesium pyrophosphate. The results are said by the authors to be satisfactory.

Mr. Cook has adopted the following method for the rapid determination of phosphorus in iron or steel: *Standard Molybdate* is made by dissolving 50 grammes of molybdate of ammonium in water, and making up to 500 cubic centimetres. Two grammes of the sample are weighed out, moistened with water, and dissolved in 7·5 cubic centimetres of nitric acid and 15 cubic centimetres of hydrochloric acid. The solution is boiled till clear, water added, the solution again boiled and then neutralised by ammonia. Five cubic centimetres of ammonia are then added, the solution boiled and then neutralised by nitric acid. Three cubic centimetres of nitric acid, and 10 cubic centimetres of molybdate are employed to precipitate the phosphorus. The liquid containing the precipitate is well shaken and allowed to stand on a warm plate for ten minutes. The precipitate is filtered from the clear supernatant liquid and washed three times with dilute nitric acid (1 to 50). The precipitate is dried, removed from the filter, and weighed. The total bulk of the filtrate and washings should not exceed 150 cubic centimetres. When the amount of phosphorus is small it is advisable to remove some of the iron before precipitating with the molybdate. The whole process can be conducted in an hour. The following analyses by Mr. Cook were made in order to compare the results obtained by this molybdic method with those obtained by the magnesia method:—

No.		Magnesia. Per cent. P.		Molybdate. Per cent. P.
1.	....	1·58	....	1·58
2.	....	1·49	....	1·50
3.	....	2·00	....	1·90
4.	....	·516	....	·52
5.	....	·620	....	·624
6.	....	·196	....	·196
7.	....	·058	....	·059
8.	....	·053	....	·059

The method as here described is of course inapplicable in the case of steel or iron containing silicon.

Mr. Stead uses the following process for estimating phosphorus in basic steel: Dissolve 2 grammes of the sample in 10 or 12 cubic centimetres of HNO_3 (sp. gr. 1·42) and 5 cubic centimetres of water. When dissolved, add 7 cubic centimetres of fuming HCl, boil, rinse the cover, and cool. The solution should measure about 30 cubic centimetres, not more than 35 cubic centimetres. Add strong NH_4HO until a slight permanent precipitate occurs; then add 7 cubic centimetres of strong NH_4HO in addition, and exactly redissolve the precipitate by cautious addition of HNO_3 to the boiling liquid; then add 4 cubic centimetres of HNO_3 (sp. gr. 1·42), and whilst the liquid is boiling hot add 12 cubic centimetres of a 10 per cent. solution of ammonia molybdate in water. Shake the liquid well and keep warm till settled, which will occur in 5 or 10 minutes. Filter off the precipitate, wash it well with water containing 2 per cent. by measure of HNO_3 (sp. gr. 1·42), dry and weigh.

If alum is added to a solution of a ferric salt and the mixture boiled with sodium thiosulphate the iron is reduced to the ferrous condition and remains in solution while alumina is precipitated. The alumina appears to carry down with it all the phosphoric acid. If the alumina is dissolved in hydrochloric acid, citric acid added, and then ammonia and magnesia mixture, a precipitate of ammonium magnesium phosphate is obtained. This method has given good results in several experiments but requires further examination.

CHAPTER IV.

THE DETERMINATION OF SILICON, SULPHUR, AND GRAPHITE.

When iron containing silicon and sulphur is dissolved in a mixture of hydrochloric and nitric acids, the silicon is converted into silicic acid or hydrated silica and the sulphur into sulphuric acid. On evaporation to dryness the silicic acid is dehydrated and becomes anhydrous silica (SiO_2), which is insoluble in nitro-hydrochloric acid. If the iron contains graphite, this is separated together with the silica. Steel usually contains no graphite, but sometimes a little carbonaceous matter is left after solution in acid. The analysis is performed upon 5 (or 10) grammes of the sample. This quantity is weighed out, and, if in borings, added a little at a time to 60 cubic centimetres of pure hydrochloric acid, free from sulphur, prepared as previously described, and 30 cubic centimetres of pure redistilled nitric acid, also free from sulphur. A crystal of pure potassium chlorate is added, and the solution evaporated to dryness on a sand bath or hot platé, and the heating continued until the residue is black. The beaker is then removed from the sand bath, and allowed to cool, and the contents moistened with the pure hydrochloric acid. Heat is next cautiously applied until the contents of the beaker are again brought down to dryness. The beaker is again cooled, and sufficient pure hydrochloric acid added to bring all the iron into solution. The solution is now slowly evaporated until a crust begins to form upon the surface. At this point the evaporation is arrested, and enough hydrochloric acid added to dissolve the crust. Only one or two drops will be required, and no more than necessary must be used. The solution is next diluted with hot water, and filtered through a Swedish filter paper, the ash of which is known. The filter retains the silica and graphite, and the sulphur is in the solution as sulphate. The solution will be basic if the directions have been complied with, the colour will be a rich mahogany, and the absence of excess of hydrochloric acid insured. Acid solutions of ferric chloride are known to dissolve small quantities of

barium sulphate. To the deep-coloured but clear filtrate about ·1 or 2 cubic centimetres of barium chloride solution are added. This reagent is made by dissolving the pure crystallised salt in about ten times its weight of water. The sulphate of barium forms in the course of a few minutes if much sulphur is contained in the sample, but in the presence of a trace only, more time is required, and in order to insure complete precipitation the solution should in all cases stand forty-eight hours after the addition of the barium chloride. After the expiration of this time it is filtered through a good Swedish filter without disturbing the precipitate, which is passed on to the filter with the last portions of the solution. The filter is well washed with cold water, then burnt in a crucible, and the barium sulphate weighed. If the ignited precipitate is white it contains no iron, and a slight pink tint may be disregarded. If the precipitate is reddish, as occasionally happens, it is necessary to fuse it for a few minutes with about six times its weight of carbonate of sodium, free from sulphate, and treat the product with dilute hydrochloric acid. In this way the original quantity of barium sulphate is reproduced, but it is now white and free from iron. The acid solution is filtered, and the precipitate washed, ignited, and weighed as before. The weight of the barium sulphate obtained multiplied by ·13734 gives the amount of sulphur present in the quantity of steel or iron taken for analysis. The residue from the first filtration, which consists of silica and carbon if obtained from cast iron, but generally of silica alone when obtained from steel, must be treated according to its composition. If no carbon is present, the filter must be dried, and the precipitate burnt and weighed. The weight of the silica multiplied by ·4667 gives the weight of the silicon. If graphite be present the contents of the filter are washed into a platinum or silver dish or crucible by the smallest possible quantity of water, and a piece of pure caustic soda added. The strong solution of caustic soda so obtained dissolves the silica. After digestion below boiling for some time the liquid is diluted and filtered. The graphite which remains in the filter is washed into a beaker and heated for a time with aqua regia. It is afterwards separated by filtration, washed, and rinsed into a crucible. The water is evaporated and the residue dried,

After weighing, the graphite should be ignited in a muffle, and the ash, if there is any, deducted from the original weight of the graphite. The caustic soda solution containing the silicon must be acidified with hydrochloric acid, and evaporated to dryness to separate silica, the residue moistened with hydrochloric acid, and again evaporated to dryness. After the vessel has been allowed to cool, water is added, and the silica filtered off, washed, ignited, and weighed. The residue left after burning off the graphite should be dissolved in acid and evaporated. If silica be present it is separated, and must be washed into the filter with the other silica from the caustic soda solution, and the whole weighed.

Although this method of evaporation with hydrochloric acid must be used for the separation of the silica and graphite before precipitating sulphur as sulphate of barium, the determinations of silica so obtained have been found by Mr. A. H. Allen to be sometimes below the truth. A more accurate estimation of silica is made by dissolving 5 (or 10) grammes of the sample in excess of pure dilute sulphuric acid and evaporating until fumes of sulphuric acid are given off. The solution is allowed to cool, diluted with water, and boiled to dissolve the crust of anhydrous ferrous sulphate. The silica is thus entirely separated, which is not always the case after evaporation with aqua regia, as confirmed by the author's experiments. The mixture of silica and graphite is filtered off, and treated as previously described. The silicon thus obtained, of course, includes any present as a constituent of slag mechanically included in the iron.

CHAPTER V.

THE DETERMINATION OF TUNGSTEN.

TUNGSTEN steel is now used in considerable quantities for various special purposes, and the estimation of tungsten in steel, and in the various sources of tungsten sold to the steel manufacturer, is therefore frequently required.

When steel is dissolved in a mixture of hydrochloric and nitric acids, and the solution evaporated to dryness, the silicon is converted into silica (SiO_2), which is a white solid. Tungsten, if present, is by the same treatment converted into tungstic anhydride (WO_3), which is a yellow solid. The tungsten, before the evaporation, is in the condition of tungstic acid, which is white, but the evaporation dehydrates the acid and forms the yellow anhydride. If the residue, after treatment with aqua regia, evaporation, and complete resolution of the iron, is lemon-yellow, or yellowish, there is more or less tungsten in the steel. The tungsten is estimated by weighing as tungstic anhydride, after separation from the silica. The analysis is conducted as described in the chapter on "The Determination of Silicon, Sulphur, and Graphite." The sample is dissolved in aqua regia, and the solution evaporated; the residue moistened with hydrochloric acid, and the liquid again evaporated. Care must be taken in each instance not to raise the mixed silicic and tungstic anhydrides to too high a temperature. The heating of the beaker on a hot plate until blackening of the residue, recommended in the absence of tungsten, would be liable to vitiate the results of the tungsten assay, by rendering some of the tungstic anhydride insoluble in ammonia. Only a gentle heating of the residue, sufficient for complete dissipation of the acid liquid, is admissible. After evaporation of the residue a second time with acid, as previously described, in order to obtain the whole of the iron in a basic solution, the silicic and tungstic anhydrides are filtered off, washed with hot water, transferred to a beaker, and digested with ammonia. The silica is not acted upon, while the tungstic anhydride is dissolved with formation of ammonium

tungstate. The liquid is filtered from the precipitate, which is afterwards washed, dried, ignited, and weighed as pure white silica. The liquid is evaporated preferably in a platinum dish, and the white residue dried in the water oven. It consists of ammonium tungstate, and must be ignited to redness, when it loses ammonia and water, and yellow tungstic anhydride remains. Should the residue, after ignition, look decidedly green, it should be moistened with strong nitric acid, and again ignited. The weight of the tungstic anhydride multiplied by ·7931 gives the quantity of tungsten in the weight of sample dissolved. The presence of tungsten in the sample therefore involves the following modification in the silicon assay:—

1. More cautious evaporation to separate silica and tungstic anhydride.

2. Treatment of the mixed anhydrides with ammonia to dissolve tungstic anhydride.

In other respects the analysis is the same as described in our last chapter.

For the analysis of tungsten ores, and the various substances containing tungsten bought by the steel-maker, for the purpose of admixture with steel, certain modifications of the above process are necessary.

The common ore of tungsten is wolfram, which is a tungstate of iron and manganese, but there is always more or less silica associated with this mineral in bulk. There are also in the market various crude substances purporting to be tungsten. Some of these contain more than 90 per cent. of the metal, others contain only 40 per cent. or so of tungsten, alloyed with iron and manganese, and associated with silicon, sulphur, and other impurities. The proper treatment of these materials varies according to the chemical composition of each. The more or less pure artificial samples of tungsten associated with silicon or sulphur, or with both, but free from quartz, should be very finely powdered and roasted in a platinum dish in a muffle at a red heat. The tungsten and silicon are thereby oxidised into tungstic and silicic anhydrides and the sulphur burnt off. The burnt residue is cooled, moistened with pure concentrated sulphuric acid, and then mixed with excess of hydrofluoric acid. On evaporation of the liquid the silicon is entirely volatilised as fluoride of

silicon. The ignited residue is fused with mixed carbonates of potassium and sodium, and the product dissolved in water and treated with nitric acid until the carbonates in excess are decomposed and a precipitate begins to form. A strong solution of calcium chloride is next added, then caustic soda solution until no further precipitate is produced. The precipitate, which consists of calcium tungstate, is filtered off, washed once or twice, transferred to a beaker, and treated with excess of strong hydrochloric acid. The calcium tungstate is decomposed and calcium chloride and tungstic anhydride are formed. The solution is diluted and filtered and the yellow anhydride well washed. It is now treated on the filter with ammonia, when it readily dissolves. The solution of ammonium tungstate is evaporated, ignited, and weighed as before described. In the analysis of wolfram and other substances containing quartz the roasting is omitted; the sample is fused with alkaline carbonate, and the solution treated as above with calcium chloride and caustic soda. The precipitate in this case contains conjugated silicic and tungstic salts of calcium, which are not decomposed by hydrochloric acid. It is therefore necessary to evaporate the calcic precipitate with hydrofluoric and sulphuric acids. The silica is thereby decomposed and volatilised, and the whole of the tungstic anhydride liberated. After evaporation to dryness without ignition, ammonia containing a few drops of ammonium oxalate is added, and the solution, which contains the tungsten, is filtered off. The necessity for this modification of the treatment in the presence of quartz is due to the fact that quartz is not entirely removed by several evaporations with hydrofluoric acid, hence it is preferable to evaporate with this reagent at a later stage, when the silica is in condition to be attacked. The treatment with calcium chloride is necessary in order to separate the tungsten from alkali, for when the solution of an alkaline tungstate is evaporated with an acid, acid tungstates of the alkali are produced, and not pure tungstic anhydride; calcium tungstate, on the contrary, is completely decomposed.

A simple qualitative test for tungsten in steel is as follows: Dissolve about a gramme of the steel in a mixture of nitric acid and phosphate of sodium, and add a piece of

zinc. The phosphoric acid keeps the tungsten in solution, and the zinc causes the appearance of a blue colour by reduction of the tungstic acid.

A method sometimes adopted is to fuse the substance with alkaline carbonate and nitrate, treat with water, neutralise the solution with nitric acid, and precipitate the tungsten as mercurous tungstate, which is filtered off, washed, and ignited. The WO_3 thus obtained is of course liable to contain SiO_2.

CHAPTER VI.

THE DETERMINATION OF CARBON BY COLOUR TEST.

Iron, as is well known, contains carbon in at least two conditions—in the free state and in combination. The carbon existing in the free state is in the form of graphite, and the estimation of this has already been described. The remainder of the carbon is chemically combined with the iron, and it is this carbon which has the principal effect in modifying the physical properties of the metal. The determination of combined carbon is frequently made by what is known as the colour-test. When iron containing combined carbon is dissolved in nitric acid certain humus-like bodies are produced, which give a brown colour to the solution, and the intensity of this colour is in proportion to the amount of combined carbon. The colour test is founded upon this property of commercial iron of forming brown solutions with nitric acid, and as it is rapid and easy of execution it is extensively used. But its value as a means of accurate estimation of carbon is very limited. It can only give correct results when the percentage is below ·6 or ·7, and it entirely fails in accuracy when the sample has been hardened.

For these reasons many experienced chemists regard the colour test as being of value only when the history of the steel is known, or in the case of mild steels made by the Bessemer process. The colour test requires the possession of samples which have been carefully standardised by the combustion process, and of nitric acid free from chlorine and diluted to the specific gravity 1·2. Several standards are required. If a Bessemer-steel has to be analysed, containing say ·6 per cent. of combined carbon, the standard employed must be a Bessemer-steel with about the same amount of carbon. If in such a case, instead of a Bessemer standard of this percentage, a crucible-steel standard, containing, say, 1 per cent. of carbon, were used, the results would probably be seriously inaccurate, and even if the crucible-steel standard were of the proper percentage of carbon, the difference in the state of

combination between the iron and carbon in the two samples, owing to their different histories, would be sufficient to produce a sensible departure from accuracy. The colour test then must be used intelligently, and the analyst must know the nature of the standards and of the samples he is analysing.

The nitric acid must be free from chlorine, because the colour of the solution, made by dissolving pure iron in nitric acid containing chlorine, is distinctly yellow, while pure nitric acid yields a practically colourless solution when of the degree of dilution required for the colour test. The details of the method are very simple. One-tenth of a gramme of the sample is weighed out into a

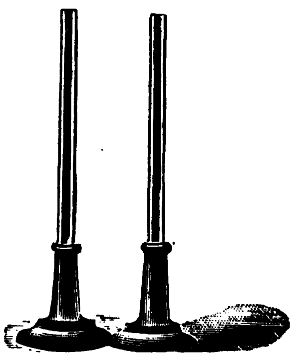

FIG. 3.

small dry test tube, and the same quantity of a suitable standard placed in a similar tube. Three cubic centimetres of the nitric acid are then measured into each test tube, and the tubes are immersed side by side, in a vessel of boiling water, for fifteen minutes. After the expiration of this time they are simultaneously removed from the boiling water, shaken so as to rinse the sides of the tube, and cooled by immersion in a vessel of cold water. The solution of the standard is now poured into one of two tubes made for this purpose, of exactly equal and uniform bore (Fig. 3) The tubes are closed at one end, and are provided with little wooden feet, on which they stand upright. One of the tubes is graduated into cubic centimetres and tenths of

cubic centimetres, and both must have been cleaned and turned upside down in their stands until dry. The solution of the standard is poured into the graduated tube and diluted with distilled water according to the amount of carbon it contains. If the standard contain ·5 per cent. of combined carbon the solution is diluted to 5 cubic centimetres; if it contain ·43 per cent. of carbon the solution is diluted to 4·3 cubic centimetres; and in the same way for other percentages. After it has been suitably diluted and shaken up, the solution is transferred to the ungraduated tube. The solution of the steel is now transferred to the graduated tube, which in the meantime has been cleaned. The last portions are rinsed in with a little water, and the two tubes are held side by side before a window, with a piece of wet filter paper behind them. Unless the percentage of carbon in the sample is less than ·3 per cent., the solution of the sample contained in the graduated tube is darker than the standard solution, and must be cautiously diluted with distilled water until they are equal. When equality in tint is reached the reading of the graduated tube gives the percentage. Each cubic centimetre equals ·1 per cent. of carbon in the sample. Thus a volume of 6·1 cubic centimetres means ·61 per cent. of carbon, and so for other readings. If the sample contain less than ·3 per cent., the solution of the standard must be doubled in volume by addition of distilled water, and the tint of the solution of the sample made equal to it. In this case half of the reading must be taken. Thus, a volume of 5 cubic centimetres means ·25 per cent. of carbon. When traces of carbon only are present the solution has a greenish tint. This can be avoided by using 2 cubic centimetres of nitric acid to dissolve both the sample and the standard. A good method, when the quantity of carbon is small, is to make use of permanent colour standards, and use a gramme of the sample. The steel is dissolved in 15 cubic centimetres of nitric acid, and the solution heated in a water-bath as before described, cooled, and filtered into a test tube of the same diameter as the standard tubes in the apparatus (Fig. 4) Between each two of these standard tubes there are holes for the insertion of the sample tube, which must be moved about until it is intermediate in tint between two

adjacent standards. There are 15 standards, representing percentages from ·02 to ·30, and the percentage on the sample can therefore be determined with an error not greater than about ·01 per cent. By taking ·5 gramme of steel and 15 cubic centimetres of acid percentages from ·30 to ·60 can be estimated; and by diluting this solution to double its volume with water percentages from ·60 to 1·20 can be determined. The permanent standards, which are made of solutions of mixed metallic salts, are standardised against Bessemer steel of known composition, and can be obtained from the makers of philosophical instruments.

THE DETERMINATION OF CARBON BY COMBUSTION.

When iron or steel is immersed in a dilute acid the iron dissolves, and the graphite is deposited as a black powder, while the greater part of the carbon previously combined with iron passes into combination with hydrogen, forming hydrocarbons, and these, being volatile, escape from the liquid.

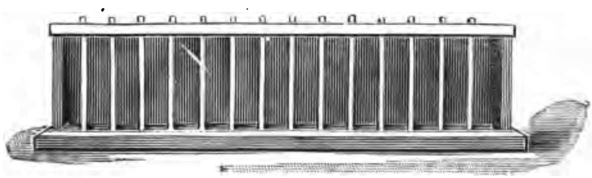

FIG. 4.

It is the various impurities—sulphur, phosphorus, and carbon—contained in iron that, by forming volatile compounds with hydrogen, cause the peculiar odour of dissolving iron. If, however, we dissolve the iron in such a way that no hydrogen is liberated no volatile hydrocarbons are formed. Such is the nature of the action when iron is placed in a solution of copper sulphate. There is here simply displacement of the copper in the sulphate by iron. The latter passes into solution, the former separates in the metallic state, and no hydrogen is liberated. All the carbon under these circumstances is deposited in the solid condition. The graphite, doubtless, is deposited in a free state, but the combined carbon forms a black substance, which resembles amorphous carbon, but contains hydrogen and oxygen. If this black mixture of carbon and carbon

compounds be filtered off and burnt it yields carbonic anhydride, which can be absorbed by caustic potash and weighed. The difference between the total carbon so determined and the graphite estimated separately is the combined carbon. These are the principles upon which the combustion process of estimating carbon is based. About 5 grammes of the steel or iron are weighed out into a beaker of 10 ounces capacity, and the beaker half filled with a solution of copper sulphate containing no free acid. The solution is made by dissolving 200 grammes of blue vitriol in water, adding caustic soda until a permanent precipitate begins to appear, then diluting to

FIG. 5.

a litre and filtering. If the sample is in the state of filings or borings solution is fairly rapid, but if a compact piece of metal has been weighed out the action proceeds slowly. In the latter case the surface should be filed before the steel is weighed; this prevents the formation of a dense skin of copper, which would delay the action of the copper salt upon the iron. The liquid may be gently warmed in order to accelerate the action, but it should not be allowed to get hot. If the solution becomes colourless more sulphate of copper solution must be added.

When the whole of the iron has dissolved, the supernatant blue liquid is decanted from the solid matter and passed through an asbestos filter. The filtration is effected with the apparatus shown in the illustration (Fig. 5) The filter-tube A is contracted at the point where it passes through the cork, and a plug of glass wool is inserted above the contraction. Upon the top of the glass wool is a filter of asbestos, which is thus made: A quantity of fibrous asbestos is ground with water until it resembles a paste; the water is then poured off and the residual felt dried, and ignited to redness in a muffle to destroy organic matter. The prepared asbestos is mixed with water, and some of the mixture is poured upon the plug of glass wool. The result is a very fine felt of short asbestos fibres, which retains the smallest particles of carbon in the subsequent filtration. The next step in the analysis is the removal of the copper, which is effected by a solution of chloride of copper containing hydrochloric acid. The chloride of copper solution is made by adding ammonium chloride to the copper sulphate solution as long as any dissolves. About 5 ounces of this reagent are poured upon the granular copper and strongly acidulated with hydrochloric acid. On digestion the copper is dissolved with formation of cuprous chloride, and the liquid becomes dark-coloured. This solution is then passed through the same filter as before, more copper chloride and hydrochloric acid are added, and the digestion continued until all the copper is dissolved. The carbon is finally transferred to the filter by means of a jet of hot water, and the filter is washed, first with boiling hydrochloric acid to dissolve insoluble compounds of copper, and then with water to free it from hydrochloric acid. The asbestos filter now contains a quantity of black carbonaceous substance, which must be burnt, and the resulting carbonic acid collected and weighed. The combustion may be effected in a stream of oxygen after the asbestos filter with its contents has been dried. But the more usual plan is to employ a moist combustion process. The accompanying illustration (Fig. 6) shows an apparatus that has been found very suitable for carbon estimations in this way. A flask A, of about 4 ounces capacity, is fitted with an indiarubber stopper, which carries a stoppered funnel tube. About 5 grammes of chromic acid crystals

are placed in this flask, and then the asbestos filter with its contents. The filter is transferred to the flask by pushing the filter-tube A (Fig. 5) down the neck, and blowing out the filter. Any carbon remaining in the filter tube must be rinsed into the flask with the smallest possible quantity of water. About 50 cubic centimetres of pure concentrated sulphuric acid are passed into the flask through the stoppered funnel, and the flask then very gently heated. The chromic acid mixture rapidly attacks the carbon, with production of carbonic anhydride, which passes out by the side tube in the neck. The gas thus evolved passes first into the tube B, where it bubbles through a solution of sulphate of silver in strong sulphuric acid, which retains any trace of chlorine, and then through

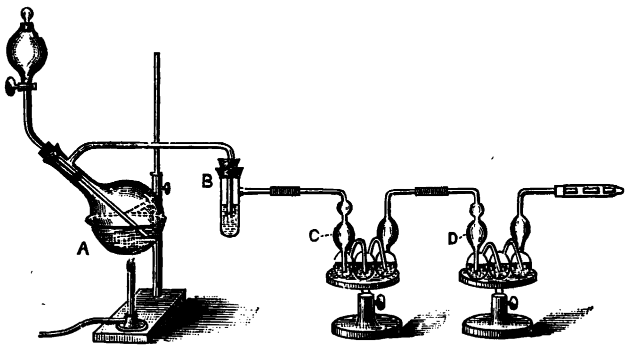

FIG. 6.

the Geissler-bulbs C, which contain pure strong sulphuric acid, which dries the gas. The carbonic anhydride next passes through the Geissler-bulbs D, which are filled with a solution of one part of caustic potash in two parts of water, and here it is absorbed. The difference in the weight of the bulbs before and after the experiment gives the weight of the gas, and this multiplied by ·2727 gives the weight of carbon. The result must be calculated to percentage. It is well to make a blank experiment with the chromic and sulphuric acids to insure the absence of organic matter in the materials, and to test the efficiency of the desiccating portion of the apparatus.

If the carbon be burnt in a stream of oxygen in the dry way, and this perhaps is a more rigorously accurate method, the manipulations are the same as are necessary in organic analysis. The oxygen is purified from carbon dioxide by passing through tubes containing pumice soaked in caustic potash, and is dried by the usual desiccating agents. The carbon dioxide and steam resulting from the combustion are passed, together with the excess of oxygen, first through a set of bulbs containing strong sulphuric acid, and then through another set of bulbs containing a solution of potash of the concentration previously mentioned. An aspirator may with advantage be used to regulate the pressure in the interior of the tube and bulbs.

Wöhler's method for the determination of carbon is used in Germany, and by some English chemists. The sample, in the state of borings, is subjected to the action of chlorine at a heat just below redness. The chlorine is evolved from a mixture of chromic and hydrochloric acids introduced into a flask previously exhausted of air by the Bunsen pump. The gas which results is free from oxides of chlorine, and is passed through a series of tubes, which remove moisture and traces of carbonic anhydride. The last tube contains phosphoric anhydride. The stream of chlorine is passed for some time through the tube until all air is removed, and the tube is filled with pure dry chlorine. The tube is then heated in the neighbourhood of the porcelain boat containing the sample, and the iron is distilled off as chloride, leaving the carbon in the form of a skeleton of the original borings. The carbon is subsequently taken out of the tube, and washed to remove chloride of manganese. It may now be burnt with a mixture of sulphuric and chromic acids in the apparatus shown in (Fig. 6), or dried and burnt in a stream of pure oxygen. In either case it is weighed in the form of carbonic anhydride.

Some chemists dissolve the iron in a solution of copper chloride neutralised by adding soda. Mercuric and ferric chloride have also been recommended for the purpose.

Mr. W. Galbraith, writing in *Iron*, calls attention to the failure of the colour test to give accurate results. In some blister steel the colour test gave 1·60 per cent. of carbon, whereas the actual amount was only ·87 per cent. as ascertained by combustion in oxygen. After hardening, he says, it is difficult to obtain the same results twice. He also points out that hammering, rolling, etc., interfere with the colour test, and suggests that the test should only be used as a comparative test in steelworks.

Mr. J. S. Parker also calls attention to anomalous results obtained by the colour test. He considers that carbon exists in steel in different conditions, and that the nature of the colouration produced by the same amount of carbon varies according to the condition in which the carbon exists.

Mr. Stead uses a modified form of the colour-test for the estimation of minute quantities of carbon. One gramme of the steel or iron is dissolved in 12 cubic centimetres of nitric acid (sp. gr. 1·2) at a temperature of 90° to 100°C. When solution has been effected 30 cubic centimetres of hot water are added, followed by 13 cubic centimetres of caustic soda solution (sp. gr. 1·27.) The colouring matter is dissolved by the soda, the intensity of the tint being 2½ times that possessed by an acid solution. The liquid is diluted to 60 cubic centimetres and allowed to stand 10 minutes. It is then filtered through a dry filter and compared with a standard which has been treated in a similar manner. Mr. Stead uses a special form of chromometer for the comparisons.

Eggertz recommends the use of 1·5 cubic centimetres of nitric acid when the percentage of carbon is small, and insists upon the necessity of diluting the solution with at least an equal measure of water before comparing, so as to destroy the greenish tint.

CHAPTER VII.

THE DETERMINATION OF CHROMIUM.

One gramme of the iron or steel containing chromium is dissolved in the usual mixture of acids, the silica separated by evaporation, and the iron and chromium precipitated by ammonia, in a porcelain dish, the reagent being added in the least possible excess and the mixture digested until the supernatant liquid is colourless. The precipitate is well washed and afterwards dried in the water oven. It is then removed from the filter paper and mixed in a platinum crucible with two grammes of potassium nitrate and four grammes of sodium carbonate, The filter paper and the adhering portions of precipitate are burnt and added to the contents of the crucible, and the mixture is fused at a red heat for half an hour. By this treatment the oxide of chromium is converted into alkaline chromate, which is soluble in water and alkalies. The fusion is boiled out with water, and digested for a few hours after addition of a few drops of alcohol. The insoluble oxide of iron is then separated by filtration and the filter well washed with hot water. The filtrate containing the chromate is acidulated with hydrochloric acid and mixed with excess of alcohol. The chromate is reduced on boiling to chloride of chromium, the colour of the solution changing from yellow to green. The excess of alcohol is removed by boiling. The slightest possible excess of ammonia is then added, and the solution is digested in a porcelain dish until the clear liquid above the precipitate is quite colourless. The chromium hydrate is thus obtained in the form of a bluish green precipitate, which must be filtered off, washed, dried, and ignited. The resulting oxide of chromium (Cr_2O_3) multiplied by ·6862 gives the corresponding weight of metallic chromium.

Instead of the fusion with alkaline carbonate and nitrate the following method may be employed: The solution in hydrochloric acid after separation of silica is mixed with a few cubic centimetres of a solution of cobalt sulphate, and then with an excess of soda and sodic hypochlorite.

Instead of adding the latter, chlorine gas may be passed into the cold liquid. On subsequent digestion the chromium becomes oxidised to chromate, and the precipitated peroxide of cobalt destroys the excess of hypochlorite by catalysis. The filtrate and washings can be treated with hydrochloric acid and alcohol or with some other reducing agent, and the chromium precipitated as hydrate and weighed as oxide, or the chromium may be estimated volumetrically by one or other of the standard methods. If a few crystals of pure potassic iodide are dissolved in the solution, and the latter then acidulated with hydrochloric acid, the liberated iodine can be titrated with standard sodium thiosulphate, or the acidulated solution of the chromate can be added to a known amount of iron in solution as a ferrous salt, and the amount of the iron remaining unoxidised determined by standard potassium bichromate. The acidulated solution of the chromate may be titrated directly against a known amount of iron, the operation being very similar to the titration of iron ores by standard bichromate.

Chromium is indicated during the determination of silicon by the sulphuric acid method, if the solution, after filtering off the silica, has a blue colour distinct from the pale green tint of the ferrous salt.

Mr. J. O. Arnold adopts the following method for the estimation of chromium in iron and steel: The sample is dissolved in hydrochloric acid, and the solution evaporated to dryness. The dry cake is fused with a mixture of sodium carbonate one part, and potassium nitrate one part. The fusion is digested with boiling water and a few drops of alcohol, and the precipitated oxides of iron and manganese, separated by subsidence and filtration. The filtrate is acidulated with hydrochloric acid and boiled with a reducing agent, and then made alkaline with ammonia. The precipitate containing chromium hydrate, and silicic acid, and alkaline salts, is then treated with hydrochloric acid, and the solution evaporated to render the silicic acid insoluble. The chromium is afterwards precipitated by ammonia and weighed as Cr_2O_3.

CHAPTER VIII.

THE DETERMINATION OF TITANIUM.

When iron or steel containing titanium is dissolved in acid in the usual method for the determination of silicon, part of the titanium remains behind with the silica, and part passes into solution. According to Riley's method the silica containing titanic acid is fused with bisulphate of potassium, and the fused mass finely ground and extracted with cold water. The titanium passes into the solution, which is mixed with the original acid solution, and the silica remains behind. The mixed solution containing the whole of the titanium is reduced with sulphite of sodium and precipitated with ammonium acetate. A small quantity of iron is allowed to remain in the ferric condition, and the titanium passes into the resulting red precipitate. The quantity of iron thus precipitated should be *as small as possible*, but the precipitate must be distinctly red. The red precipitate is dried and fused with potassium bisulphate, and the solution of the fusion in cold water is nearly neutralised and boiled for some hours. The precipitated titanic acid is filtered off, after standing some hours in a warm place, washed with dilute sulphuric acid, dried, ignited, and weighed as quickly as possible. It is advisable to add a little sulphurous acid, before boiling to precipitate the titanic acid, as iron in the ferric condition has a tendency to prevent the precipitation. After filtering off the titanic acid it is advisable to neutralise still further and boil again to ensure that no titanium is left in solution. The weight of titanic acid (TiO_2) multiplied by 0·60 gives the corresponding weight of metallic titanium. Another method of determining titanium is to treat the sample with acid and separate the silica and part of the titanic acid. The mixture is afterwards evaporated with sulphuric and hydrofluoric acids. The silica is volatilised, while the titanic acid is fixed in presence of sulphuric acid. The original acid solution is reduced by sulphite of sodium, and the remainder of the titanic acid precipitated, as in Riley's method. The

red precipitate and the residual titanic acid from the silica are mixed and fused with potassium bisulphate, the fusion treated with cold water, and the solution boiled to precipitate titanic acid. If it be desired to determine phosphoric and titanic acid on the same quantity of sample, the red precipitate may be dissolved in hydrochloric acid, and citric acid and ammonia added. The phosphoric acid is then precipitated by magnesia mixture and the precipitate filtered off. The iron in the filtrate is removed by ammonium sulphide, and the solution thus freed from iron is evaporated down and the residue ignited to destroy organic matter. This residue and the original silica containing part of the titanic acid are mixed, fused with potassium bisulphate, and the titanic acid precipitated by boiling as before described.

Mr. Edward Jackson some years ago communicated to the author the following method of testing for titanium: The iron is dissolved in nitric acid, the solution evaporated down, and the residue digested with strong sulphuric acid, or fused with potassium bisulphate. The titanic acid is dissolved in cold water in the usual way and peroxide of hydrogen added, when, if titanium is present, a yellow colouration appears, which is due to a higher oxide of titanium (probably TiO_3) since described by Weller and also Piccini.

Probably this reaction might be made the basis of a rapid colorimetric determination of titanium.

CHAPTER IX.

THE DETERMINATION OF NITROGEN, OXYGEN, SLAG, ETC.

MR. A. H. Allen uses the following method for the determination of nitrogen in iron and steel: One gramme of the sample is weighed out and heated to incipient redness in a porcelain crucible. While still hot it is dropped into the flask A (Fig. 7), which contains a small quantity of ammonia-free water. The cork F is next inserted

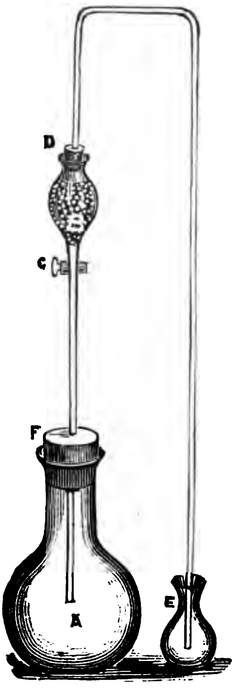

FIG. 7.

and with it the tapped bulb and the tube B C. B contains a number of recently ignited glass beads. The water in the flask is then boiled for some minutes till steam issues copiously from the open top of B, and the air is judged to have been completely expelled. The tap C is then closed and the lamp removed from under A. As

the cooling proceeds the flask becomes vacuous, through condensation of the steam, and any trace of air contained in the pores of the cork, or elsewhere, is removed by subjecting the water in the flask to a second boiling, followed by closure of the tap.

Twenty c.c. of hydrochloric acid (sp. gr. 1·10) are next poured into the bulb B, and the bent tube and india-rubber cork D inserted. The tube is at least three feet in vertical height, and the lower end is closed by mercury. The acid in B is next boiled until all the air is expelled through the mercury, when the tap C is opened and the acid runs into the flask. By operating in this manner the metal may be dissolved without admitting the smallest quantity of air or the loss of the least trace of the ammonia formed. When the solution of the metal is complete the source of heat is withdrawn and the tap closed. The long tube is removed, water poured into the bulb and allowed to enter the flask by opening the tap. The contents of the flask are then transferred to a larger flask, or retort, adapted to a Liebig's condenser, and excess of freshly-burned finely-powdered quicklime added, and the liquid distilled. In the distillate the ammonia is determined by Nessler's reagent in the same manner as in a water analysis. Mr. Allen says that experiment has conclusively proved that the presence of air during the solution of the metal does not cause any formation of ammonia, and he therefore considers the foregoing precautions for the exclusion of air during solution of the steel not essential to the accurate performance of the analysis. A number of experiments made by this method on steels of varying nature show percentages of nitrogen varying from ·004 to ·017.

Messrs. Drown and Shimer, as also Mr. Watts of Birmingham, separately determine the silicon and the slag existing in iron by a modification of Wöhler's method for carbon. A portion of the sample is subjected in the usual way to the action of chlorine, and the residual carbon washed and burnt in a stream of oxygen. Another portion of the sample is submitted to pure dry chlorine—in a combustion tube, the exit end of which is bent, but not contracted, and dips into water contained in a flask. The slag is not acted upon by the chlorine, and remains behind with the carbon, while the silicon existing in a non-oxidised condition is volatilised as chloride, with the excess ot chlorine. The silicon chloride passes into the water, and is decomposed with formation of silicic acid, which is obtained as insoluble silica by evaporation to dryness. The residue remaining in the boat is slag *plus* carbon, and the carbon having been determined by a separate operation, the percentage of slag is easily obtained. The carbon may also be burnt off, and the residual slag is then obtained by direct weighing. Mr. Watts gives the following results and a description of the details in the *Chem. News*, of June 30th, 1882 :—

	Description of Iron.	Percentage of Slag.	Percentage of Silicon.
Cast Irons.—			
I.	White Staffordshire	0·74	0·64
II.	No. 1 Haematite	0·07	2·21
III.	No. 1 Blast Staffordshire	*4·40	3·96
IV.	No. 2 ,, ,,	0·62	3·09
V.	No. 3 ,, ,,	0·84	4·09

* This appears to be exceptionally high.

Mr. W. Bettel determines the basic cinder and oxides in iron by treating the sample in the state of borings with a solution of bromine and potassic bromide in water. The residue is washed with dilute sulphuric acid, containing 5 per cent. of hydrochloric acid, then with dilute hydrochloric acid (·5 per cent.), and finally with water. The silica is extracted by boiling with sodium carbonate. As an alternative method the same author proposes the solution of the sample in cuprous chloride, mixed with potassium chloride and dilute hydrochloric acid (1 in 20). The residue is washed free from copper with potassium chloride solution, then with hydrochloric acid (1 in 50), and finally with hot water, and the silica separated as before.

Professor A. Ledebur, of Freiburg, determines oxygen in iron and steel as follows:—

The sample in the state of borings is dried at 200° C in a current of pure nitrogen. About fifteen grammes are then placed in a glass tube in a porcelain boat, and a current of pure nitrogen, dried by passing over phosphoric anhydride, is passed through the tube to displace air and remove moisture from the warmed sample. A weighed absorption tube containing phosphoric anhydride is then attached, and a current of pure hydrogen, dried by passing over phosphoric anhydride, is passed through the apparatus for forty-five minutes, the sample being kept at a red heat. The oxygen is converted into water, which is absorbed by the phosphoric anhydride. The following are some of the results obtained:—

DESCRIPTION.	First Experiment.	Second Experiment.	Third Experiment.
Grey Pig Iron	·000	·000	—
Martin Iron from Oberhausen	032	·035	—
Ingot Iron—Bochun	053	·042	—
Thomas Metal before complete dephosphorisation	·069	·068	—
Thomas Metal after dephosphorising, before adding spiegel	·126	·111	—
Puddled Iron, Gutchoffnungs — Hütte	·507	·515	·524

SPECTROSCOPIC EXAMINATION OF IRON AND STEEL.

Messrs. Parry and Tucker have dissolved 7,000 grains of Bessemer steel in aqua regia for examination by the spectroscope. The solution was evaporated to dryness and heated to 250° C for some time, until all the acid was driven off. Ammonia of sp. gr. ·880 was then poured on, and caused to act under pressure for several days. The ammonia was then filtered off, and evaporated to dryness with nitric acid, to decompose any ammonium salts. The residue was treated with hydrochloric acid, and its spectrum photographed, when the presence of nickel, cadmium, copper, calcium, and manganese was recognised.

The original residue from the evaporated solution of the iron was then heated with water, no new elements were extracted. It was then boiled for some time with acetic acid, some of the iron was dissolved, the solution was therefore nearly neutralised with ammonia and boiled. Photographs were taken of the spectrum of the iron so precipitated, and the filtrate from it. The former showed nothing but an increase of manganese, while the latter gave lines corresponding to lead, aluminium, chromium, manganese, and calcium.

The same authors have since reported to the Iron and Steel Institute, that they are continuing their researches, and are obtaining results of interest by direct examination of the spectra, without solution of the iron.

Mr. F. A. Emmerton has described the methods of analysing steel in use in the laboratory of the Joliet Steel Company, in a paper read (October, 1881), before the American Institute of Mining Engineers.

For *Carbon*, the Eggertz colour test is used, the standards employed being made by dissolving burnt sugar and burnt coffee in water.

For *Silicon*, what is essentially Dr. Drown's method is used. The solution is made in a mixture of one part concentrated sulphuric acid, and four parts of nitric acid of 1·2 sp. gr.

For *Sulphur*, Elliot's method of conducting the sulphurretted hydrogen, formed during the solution of five grammes of the steel in hydrochloric acid, through a solution of caustic potash. The sulphide formed is afterwards titrated with standard iodine.

For *Phosphorus*, 10 grammes of steel are dissolved in nitric acid, the solution evaporated to dryness, the residue dissolved in hydrochloric acid, the solution diluted, and mixed with excess of ammonia. The precipitated hydrate of iron is redissolved in nitric acid, and 80c.c. of molybdate solution added. The precipitate, after standing four hours, is dissolved in ammonia, and the phosphoric acid precipitated by magnesia mixture.

For *Manganese*, Volhard's method is used (see page 11).

M. Troilius in a paper submitted to the American Institute of Mining Engineers, remarks on the necessity of uniform standard methods for the analysis of iron and steel. After a special study of the methods in use in England and abroad he recommends

Eggertz's method for *carbon* determination.
Eggertz's molybdic acid method for *phosphorus*. (The phosphorus to be weighed as phospho-molybdic acid.)
The aqua regia and sulphuric acid methods for *silicon*.
Riley's method by acetate of ammonium and bromine for *manganese*.
The method of solution in aqua regia and separation of silica by evaporation with subsequent addition of barium chloride for *sulphur*.

CHAPTER X.

ANALYSES OF IRON AND STEEL.

Analyses showing that the elements are not evenly distributed in an ingot. (G. J. Snelus.)

	Drilling from Top of Ingot.	Drilling from Bottom of Ingot.
Iron	98·304	99·038
Combined Carbon	·760	·350
Silicon	trace	trace
Sulphur	·187	·044
Phosphorus	·191	·044
Manganese	·558	·514
	100·000	100·000

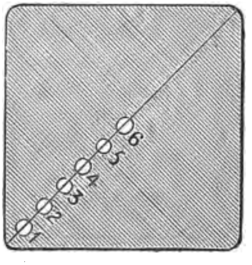

FIG. 8.

	Drilling from Section at Top.			Drilling from Section at Bottom.		
	C. Cab.	Sulp.	Phosp.	C. Carb.	Sulp.	Phosp.
1.	·44	·032	·044	·44	·048	·060
2.	·54	·048	·060	·42	·056	·062
3.	·57	·080	·086	·41	·048	·054
4.	·61	·096	·097	·40	·048	·054
5.	·68	·120	·111	·38	·048	·058
6.	·77	·187	·142	·37	·044	·052

Steel used for dies in the Royal Mint:—

	A.	B.	C.	D.
Iron	98·93	98·63	98·64 by diff	98·07
Carbon	0·82	1·07	0·79	1·19
Manganese	0·10	0·12	0·24	0·45
Silicon	0·05	0·06	0·18	0·29
Sulphur	trace	trace	0·01	trace
Phosphorus	——	trace	0·01	trace
Copper	——	——	0·02	——

Bessemer metal submitted to the War Department for purposes of ordnance, etc.—

Silicon	0·00
Graphite	0·00
Combined Carbon—Minute Quantity.	
Sulphur	0·02
Phosphorus	trace
Manganese	trace

Steel considered by the Swedish Ordnance Commisson the most suitable for barrels of cannon—

Carbon	0·35 to 0·45
Silicon	0·40 to 0·60
Manganese	0·40 to 0·60
Phosphorus	under 0·06

Analyses of steel supplied by various firms to the Royal Gun Factory, Woolwich :—

Maker.	Carbon.	Manganese.
Firth	0·338 0·400	0·075 0·126
Whitworth	0·300 0·417	0·312 0·240
Vickers	0·240 0·272	0·216 0·225
Cammell	0·143 0·194	0·341 0·248

The analyses bracketed together are analyses of different samples.

Steel highly approved by the Swedish Government for the barrels of guns :—

Carbon	0·470
Silicon	0·443
Manganese	0·410
Sulphur	0·039
Phosphorus	0·083

Steel made without blow-holes by the use of silicide of manganese for barrels of Russian cannon :—

Carbon	0·120
Silicon	0·234
Manganese	0·527
Sulphur	0·020
Phosphorus	0·109

Analysis of steel taken from a Krupp cannon supplied to Austria :—

Carbon	0·405
Silicon	0·191
Phosphorus	0·032
Sulphur	0·023
Manganese	0·184
Cobalt and Nickel	0·057
Copper	0·126
Iron (by difference)	98·982
	100·000

Ideal composition of steel rails according to Mr. Dudley:—

Carbon	·300
Silicon	·040
Phosphorus	·100
Manganese	·350

Ideal composition of steel rails according to Mr. Snelus:—

Carbon	·350
Silicon	·100
Phosphorus	not more than ·075
Manganese	·750

Analysis by Herr Wasum, showing the effect of copper and sulphur on the working qualities of steel for rails:—

Charge	C.	Si.	P.	Mn.	S.	Cu.	Rolling qualities.
INFLUENCE OF COPPER.							
No. 1.	·276	·144	·064	·778	·059	·452	Very good.
No. 2.	·233	·091	·050	·709	·060	·862	Good.
INFLUENCE OF SULPHUR.							
No. 3.	·280	·160	·049	·634	·119	·050	Good.
No. 4.	·393	·141	·065	·695	·158	·040	Good.
No. 5.	·258	·136	·043	·500	·201	·076	Bad.
No. 6.	·307	·075	·039	·488	·214	·057	Bad.
No. 7.	·224	·089	·030	·480	·231	·066	Very bad.
INFLUENCE OF COPPER AND SULPHUR.							
No. 8.	·311	·051	·061	·514	·107	·859	Good.
No. 9.	·281	·169	·059	·594	·170	·429	Bad.
No. 10.	·235	·164	·045	·468	·173	·573	Bad.
No. 11.	·262	·131	·052	·655	·189	·406	Bad.

Analyses quoted by Mr. Sergius Kern of steel containing copper used in the manufacture of excellent Krupp guns:—

	I.	II.	III.	IV.	V.
Combined Carbon	0·56	0·64	0·42	0·50	0·69
Graphite	0·04	0·04	0·04	0·02	0·02
Silicon	0·19	0·10	0·11	0·09	0·06
Manganese	0·18	0·16	0·13	0·07	0·15
Phosphorus	traces.	traces.	nil.	nil.	traces.
Sulphur	—	—	—	—	—
Copper	0·27	0·35	0·30	0·35	0·26

At the Cockerill Works at Seraing, all steel not found to come within the following limits is rejected as unfit for shipbuilding:—

Carbon	0·08	0·15
Silicon	trace	0·02
Sulphur	0·03	0·05
Phosphorus	0·03	0·05
Manganese	0·30	0·60

Analyses quoted by Mr. Sergius Kern, showing that excess of silicon in presence of excess of carbon is injurious.

Steel used for tyres, axles, and steel plates for bridges:—

	Bad Steel.			Good Steel.		
	1.	2.	3.	1.	2.	3.
Combined Carbon and Graphite	0·53	0·70	0·40	0·49	0·72	0·35
Silicon	0·64	0·61	0·59	0·01	0·06	0·05
Phosphorus	0·03	0·01	0·01	0·03	nil	nil
Sulphur	0·06	nil	0·01	0·03	0·01	nil
Manganese	0·55	nil	nil	0·57	nil	nil
Copper	0·03	nil	nil	0·02	nil	0·01

Analyses made at Landore showing the amount of sulphur in pig iron and the steel made from it by the open hearth process:—

Name of ore used.	Sulphur in pig iron per cent.	Sulphur in finished steel per cent.
Elba	0·025	0·032
Marbella	0·025	0·064
Sommorostes	0·025	0·025
Mockta	0·025	0·025
Tagus	0·025	0·064
Soumah	0·025	0·048

Results quoted by Mr. Spencer, showing the influence of hardening and annealing upon the condition of carbon in steel:

No. 1 sample.	Before Hardening.	Hardened.	Annealed.
Combined C. (Colour Test)	·89	·58	·98
Graphitic Carbon	·29	traces	·20
Total Carbon (Col. Test + Graph.)	1·18	·58	1·18
Total Carbon by Combustion	1·18	1·09	1·20
		Loss ·51	
No. 2 sample.			
Combined C. (Colour Test)	·80	·66	·79
Graphitic Carbon	·34	·07	·44
Total Carbon (Col. Test + Graph.)	1·14	·73	1·23
Total Carbon by Combustion	1·21	1·10	1·19
		Loss ·37	
No. 4 sample.			
Combined C. (Colour Test)	·38	·22	·38
Graphitic Carbon	·04	none	traces.
Total Carbon (Col. Test + Graph.)	·42	·22	·38
Total Carbon by Combustion	·39	·34	·38
		Loss ·12	

The "loss" in these analyses refers to carbon not existing as graphite, and not detected by colour test. See remarks by Messrs. J. S. Parker and Galbraith.

Bessemer steel made at Seraing, and said to be as soft as Swedish steel from Witkowitz:—

	Plate No. 1.	Plate No. 2.	Square Bar.	Round Bar.
Silicon	0·000	0·000	0·000	0·000
Carbon	0·040	0.090	0·060	0·070
Sulphur	0·010	0·010	0·010	0·010
Phosphorus	0·008	0·014	0·011	0·000
Manganese	0·290	0·290	0·260	0·360

A sample of very pure dephosphorised metal made by Mr. Snelus:—

Silicon	·019
Sulphur	·030
Phosphorus	·003

Analyses by Mr. W. H. Johnson of different samples of steel wire, with determinations of electrical resistance in ohms per metergram:—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 7.	No. 8.
Iron	98·980	99·070	98·870	98·880	99·030	99·170	99·007
Comb. Carbon	0·391	0·438	0·270	0·280	0·182	0·226	0·268
Graphitic Carbon	0·040	0·060	0·150	0·150	0·130	0·050	0·080
Silicon	0·157	0·011	0·190	0·150	0·140	0·080	0·033
Manganese	0·088	0·300	0·470	0·410	0·390	0·340	0·380
Sulphur	0·080	0·031	trace	trace	trace	trace	trace
Phosphorus	0·096	trace	trace	trace	trace	trace	trace
Comb. C + Si + S + P.	0·724	0·479	0·460	0·430	0·322	0·306	0·301
Electrical Resistance	2·140	1·903	1·560	1·519	1·450	1·430	1·070

Analysis of New British Iron Co.'s "Lion" wrought iron (ordinary), by Mr. J. H. White:—

Combined Carbon	0·21
Silicon	0·13
Phosphorus	0·13
Sulphur	trace
Manganese	nil

Analysis of New British Iron Co.'s "Corngreaves" cold blast pig, grey No. 4, by Mr. J. H. White:—

Carbon (graphite)	2·916
Silicon	1·540
Phosphorus	0·460
Sulphur	0·088
Manganese	1·190

Analysis of New British Iron Co.'s "Lion" pig, No. 4, by Mr. J. H. White:—

	(1)	(2)
Graphite	3·93	3·80
Silicon	1·61	1·46
Phosphorus	0·48	0·53
Sulphur	0·074	0·086
Manganese	0·69	0·57

Analyses of spiegeleisen by Mr. Edward Riley:—

	I.	II.	III.	IV.	V.	VI.
Iron	88·378	86·713	85·507	83·777	81·111	80·581
Manganese	6·984	8·448	9·856	11·782	13·689	14·770
Carbon	4·176	4·071	4·501	4·538	4·443	4·164
Silicon	·245	·629	·248	·041	·476	·096
Sulphur	·100	·039	·041	·010	nil	trace
Phosphorus	·037	·483	·098	·084	·212	·365
Copper	·424	·102	trace	·015	·080	trace
	100·344	100·485	100·251	100·247	100·011	99·976
Total of elements other than Fe and Mn.	4·982	5·324	4·888	4·688	5·211	4·625

CHAPTER XI.

THE ANALYSIS OF IRON ORES, SLAGS.

For many purposes it is sufficient to know the total amount of iron in an ore, but very often an extended investigation to determine the amount of the other bases, and of the phosphorus, sulphur, and silica, and the titanic and carbonic acids is necessary. Sometimes the knowledge of the relative proportions of the various acids and bases in a slag is of importance in explaining irregularities in the working of the blast furnace and suggesting remedies, and since the quality of the iron depends very largely upon the composition of the ore, and of the other ingredients forming the charge of the furnace, the analysis of ores, slags and fuels is constantly demanded of the chemist.

The Determination of Iron.—When the determination of the total iron, irrespective of its state of oxidation, is required, it is simply necessary to dissolve the ore (or slag), and bring the iron into the state corresponding to it lowest oxide (FeO). A suitable reagent is then added which converts the ferrous salt into ferric salt, corresponding to the oxide Fe_2O_3, and the quantity of the oxidiser used is a measure of the total iron.

The reagent which has been found most suitable, and which has best withstood the test of experience is potassium bichromate. Potassium permanganate is also employed, but the strength of the solution is not constant, and special precautions must be taken in presence of hydrochloric acid. One gramme of ore or several grammes of slag in a state of fine powder, should be weighed out for the analysis. If the substance is capable of being decomposed by boiling with strong hydrochloric acid, this reagent should be employed in fairly large excess. The solution is performed in a strong flask of 300 cubic centimetres capacity, fitted with a cork or caoutchouc stopper, which carries a bunsen valve opening outwards (Fig. 9). This valve prevents air entering the flask, but permits the easy passage of gases and vapours out of it. The flask is placed upon an iron plate or sand bath, and the

contents boiled until the ore is completely decomposed. This may be known by the appearance of the residue, which consists of white silica unless organic matter is present. During the digestion with strong acid, the stopper and valve may be removed, and the mouth of the flask partially closed by a small funnel which condenses the greater portion of the acid, and prevents mechanical loss of the solution.

FIG. 9.

After the decomposition, the solution is diluted with water to about 200 cubic centimetres, a piece of metallic zinc, free from iron, is immersed in it, and the cork and valve are placed in position. The zinc dissolves in the acid, and the iron is reduced to the ferrous state. The digestion with zinc should take place at a gentle heat, and the flask should occasionally be subjected to a rotary motion to mix the solution. At the time of adding the zinc about a gramme of sodium bicarbonate should be dropped into the flask; the resulting carbonic acid expels the greater part of the air, and the remainder is expelled by the hydrogen, so that the reduction of the iron takes place in an atmosphere free from oxygen. If the liquid is boiled during the reduction, the zinc is dissolved too rapidly and therefore uselessly, and at the same time the steam drives

out the hydrogen. Afterwards, when the flask cools and the steam condenses, a vacuum is produced which endangers the flask, and threatens loss of the analysis.

When all the iron is reduced, and the hot solution appears quite colourless, the liquid should be cooled and tested by potassium sulphocyanate. If a drop of the liquid and a drop of a dilute solution of sulphocyanate give no colouration, or only an extremely faint trace of pink when mixed, the reduction may be considered complete. Ferrous salts are colourless when mixed with the sulphocyanate, but it is difficult, by reduction with zinc, to remove the last trace of ferric salt. If the amount of colouration does not exceed a faint trace of pink, the quantity of ferric salt is insignificant, and may safely be neglected. All the zinc should be dissolved before the liquid is removed from the flask, as portions of iron are liable to be deposited on it, and to escape solution as long as any zinc remains. The quantity of zinc to be added is known after a little experience. The titration is performed by a standard solution of potassium bichromate, with potassium ferricyanide as indicator. The bichromate is added from a burette to the solution contained in a capacious porcelain dish, in presence of a good excess of free acid. A drop of the solution is from time to time taken on a glass rod, and mixed with a very dilute solution of the ferricyanide on a white tile. At first a deep blue colouration results, but as more and more bichromate is run in, and fresh trials are made, the colouration becomes fainter. The reagent must be finally added drop by drop, and the liquid tested each time. As soon as all the iron is oxidised the drop gives no trace of blue colouration; the reaction is so sensitive that the reading may be made to a tenth of a cubic centimetre. The ferricyanide must not give a blue tint when mixed with a drop of dilute ferric chloride, that is to say it must be free from ferrocyanide. The standard solution of bichromate is conveniently of such a strength that one cubic centimetre equals one per cent. of iron when one gramme of the sample is used. Pure potassium bichromate, dried by cautious fusion, or in an air bath, is dissolved in water in the proportion of 8·777 grammes per litre. The strength of this standard solution should be checked by titration with a known amount of iron. A

sample of iron, of which a complete analysis has been made, may be kept for the purpose. A quantity of this, corresponding to a gramme of pure iron, is dissolved in dilute sulphuric acid, together with a small piece of pure zinc in a flask similar to that used to dissolve ores. The solution is transferred to a procelain dish, and 95 cubic centimetres of the standard bichromate at once run in. If a blue tint is obtained with ferricyanide, the addition of bichromate is continued cautiously until the two drops no longer give a trace of blue. If exactly 100 cubic centimetres of bichromate are required, the standard solution is of exact titre, if either more or less than 100 cubic centimetres are necessary to complete the reaction, the solution may be evaporated or diluted to the exact volume, or a factor may be calculated and written on the label. Tables have been published which dispense with multiplication when the factor is once found.

In presence of titanic acid it is advisable to reduce the iron with sulphuretted hydrogen; the strong flask (Fig. 9) serves for this purpose. The acid solution containing the ferric iron is placed in the flask, the stopper and valve being removed, and a stream of snlphuretted hydrogen is passed into the solution. The iron is reduced to the ferrous state, but the titanic acid, which is reduced by zinc in acid solution; remains unchanged. The liquid is thus saturated with sulphuretted hydrogen, which has to be removed by boiling. The stopper and valve are accordingly placed in position, and the solution boiled until the steam issuing from the valve fails to darken a piece of filter paper, wetted with lead acetate solution. The liquid after cooling is tested with potassium sulphocyanate for ferric iron, and titrated with potassium bichromate or permanganate. Instead of sulphuretted hydrogen sulphur dioxide may be employed to reduce iron; and these reagents may be employed instead of zinc in the absence, as well as in the presence of titanic acid, but zinc in ordinary instances deserves the preference.

CHAPTER XII.

THE TREATMENT OF INSOLUBLE SAMPLES AND THE DETERMINATION OF PROTOXIDE OF IRON.

MANY ores and slags are not decomposed by boiling with hydrochloric acid, and it becomes necessary to adopt other means of effecting solution.

Ores of this class are usually decomposed when heated with fuming hydrochloric acid, under pressure, in a sealed tube. The sample is very finely powdered and weighed out into a tube of glass closed at one end. The required amount of fuming hydrochloric acid is then placed in the tube, which is drawn off to a thick neck and sealed. The glass should be soft enough to allow of the ends of the tube being made as thick as the other portions. The tube with its contents is then wrapped in wire gauze and heated for an hour or two in the water oven, or if necessary in a calcium chloride or sodium nitrate bath, or to 200° C. in an air bath. Shaking at intervals assists solution. When the ore is decomposed the tube is allowed to cool and cautiously opened, and the liquid transferred to a flask. The iron can now be reduced with zinc, and titrated with standard bichromate.

Another method of decomposing the sample is by fusion with potassium bisulphate. The finely ground ore or slag is mixed with several times its weight of the bisulphate, and a few drops of strong sulphuric acid, in a capacious platinum crucible. The crucible is covered and heat cautiously applied to cause the contents to fuse; the molten mass is occasionally stirred with a platinum rod, and particles of undecomposed ore clinging to the sides of the crucible are pushed down. The heat is continued until, by the appearance of the mass, it is judged that all the ore is decomposed, the crucible is then grasped firmly by the tongs, removed from the source of heat, and rapidly rotated while the fused matter solidifies. This causes the mass to set in a thin stratum upon the walls of the crucible, and when it is cold the cake can be loosened by judicious

squeezing. The fusion, which is yellow when hot, but almost white when cold, is dissolved in water containing hydrochloric acid, reduced with zinc and titrated.

Fusion with alkaline carbonate is another way of decomposing an ore or slag. The sample, quite free from gritty particles, is thoroughly incorporated with five times its weight of pure sodium carbonate in a platinum crucible, and the mixture is fused in a muffle or over a blast lamp.

The mixture effervesces at first owing to the escape of carbon dioxide, but afterwards fuses calmly. It is well stirred from time to time, and then cooled in the manner

FIG. 10.

described for the bisulphate fusion. The mass is transferred to a covered beaker, and treated with water and afterwards with hydrochloric acid. Silica is separated, and becomes insoluble on evaporation, while the iron is dissolved. The evaporation with acid in the first instance should be conducted to complete dryness. The dry matter after cooling should be again treated with hydrochloric acid (sp.

gr. 1·1), and the evaporation continued, but not to dryness. On adding water and boiling, the silica remains insoluble, while the iron passes into solution.

Siliceous ores, and slags, may be decomposed with hydrofluoric acid with great ease. The fine powder is spread on the bottom of a platinum dish, and made into a paste with pure sulphuric acid. The dish is then three parts filled with hydrofluoric acid, and heated in the draught cupboard over a small flame. As the liquid evaporates the silicate is decomposed, and silicon fluoride is volatilised. If necessary the treatment with hydrofluoric acid is repeated, but the final evaporation is continued until sulphuric acid fumes are formed in abundance. The residual acid solution is cooled, digested with dilute hydrochloric acid, and then further diluted with water. The iron is next reduced with zinc, and titrated with bichromate.

The determination of iron existing in an ore as protoxide is effected by bringing the ore into solution with exclusion of air or oxidising materials. If the ore is decomposable by acids, it is dissolved in hydrochloric acid that has been previously boiled to eliminate air. The ore is placed in the flask *a* (Fig. 10), and the proper quantity of recently boiled hydrochloric acid poured upon it. About a gramme of sodium bicarbonate is dropped into the flask, which is then closed by a cork bearing an evolution tube (*b*), provided with a pinch tap (*c*). The second limb of the evolution tube dips beneath the surface of the recently boiled water in (*d*). The flask is gently heated to boiling until the ore is decomposed, the lamp is then removed, and the liquid allowed to cool. The cooling causes a decrease of pressure, and the water in (*d*) is sucked over into (*a*). The clip is closed in time to prevent air entering into (*a*), and the liquid is left to cool, and subsequently titrated with bichromate. The iron so found is that which originally existed in the ore in a state of protoxide.

The method of decomposition in a sealed tube is very convenient when the protoxide of iron has to be determined in insoluble samples. During the decomposition air has necessarily no access, and the iron remains in the state in which it originally existed. The titration is made as soon as the tube has been cooled and opened, and the percentage of protoxide of iron obtained at once. The

treatment with hydrofluoric acid is also adapted for the estimation of protoxide of iron. The details of the experiment are as previously described, but the platinum dish is heated upon a water bath, and a ring of plaster of Paris several inches deep surrounds it. The ring is furnished with a slab of plaster to act as a lid, and through a hole in the latter a glass tube conveying a current of carbonic anhydride is passed. The solution of the iron thus takes place in an atmosphere incapable of oxidising the iron. When the ore is decomposed and the hydrofluoric acid evaporated, the dish is removed from the water bath, and the liquid diluted and titrated.

In all titrations of iron with oxidising reagents the analyst should bear in mind that solutions made with sulphuric acid are generally to be preferred to those made with hydrochloric acid. For this reason many chemists use a mixture of sulphuric acid three parts and water one part, instead of fuming hydrochloric acid, for decomposing ores in a sealed tube. Sulphuric acid solutions containing iron in the ferrous condition are less easily altered by absorption of oxygen from the air than are solutions made with hydrochloric acid, but the latter do not sensibly alter during the exposure necessary for the performance of the titration.

CHAPTER XIII.

THE DETERMINATION OF MOISTURE AND COMBINED WATER.

THE moisture in an ore is determined by drying at the temperature of boiling water. Twenty grammes of the well-sampled and coarsely-ground ore are weighed into a shallow dish, which is then placed in the water oven and weighed from time to time until the weight is constant. The dried sample so obtained should at once be placed in a stoppered bottle and reserved for the determination of the other constituents of the ore.

The sample dried at 100°C. is, in most instances, still capable of losing water when raised to a high temperature; the water thus eliminated is termed "combined water." For some purposes it is sufficient to ignite the ore to redness in a platinum crucible, and express the loss as "combined water and organic matter," after making a correction for the loss of carbonic acid and for the oxidation of protoxide of iron. If the amount of combined water is required to be known with greater accuracy than can be attained in this way, one or two grammes of the ore are heated to redness in a tube of hard glass, to which a previously weighed calcium chloride tube is attached. The tube is drawn off at the closed end in the usual manner, and after the experiment this end is broken and a current of air, dried by passing over calcium chloride or soda-lime, is aspirated through the tube to remove the aqueous vapour from the interior. The increase in weight of the calcium chloride tube, multiplied by 100 or by 50, according to the amount taken, gives the percentage of combined water. The tube used in the experiment must, of course, be perfectly dry, the cork should be dried in the water oven. The tube may be heated in a combustion furnace, or, in default of this, over a good burner. When the combined water and organic matter are determined by simple ignition to redness in an open crucible, the carbon acid is expelled and the protoxide of iron becomes oxide of iron. The percentage of oxygen absorbed, calculated from the known amount of protoxide of iron, is added to the loss on ignition,

and the percentage of carbonic acid is deducted. The result is the "combined water and organic matter." Slags, as might be inferred from their origin, contain no combined water or organic matter.

THE DETERMINATION OF CARBONIC ACID (CO_2).

The determination of carbonic acid in iron ores is made by the usual process. The ore is treated with acid and the weight of the resulting carbonic anhydride ascertained.

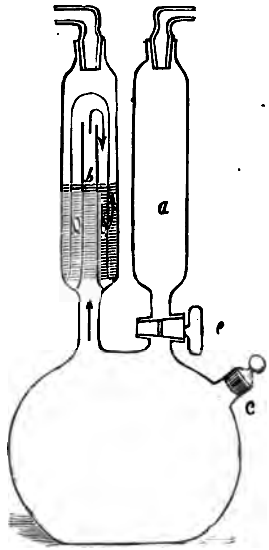

FIG. 11.

The usual method is to weigh the ore and acid, and the vessel containing them, before the reaction takes place, and again after the reaction, when the carbonic anhydride has escaped into the air. The difference between the two weighings, of course, gives the carbonic anhydride. Many forms of apparatus have been devised for the execution of the experiment, Schrötter's apparatus, which is very convenient, may be taken as a type of all. This apparatus (Fig. 11) is essentially a small flask with two elongated necks. One of the necks (*a*) is contracted at the point of union with the body of the flask and has a stopcock on the narrowed portion. The mouth of this neck is also

narrowed and is closed with a stopper; the stopper may conveniently be perforated as shown. At the commencement of the analysis this neck contains the acid. The other neck is so contrived that the gas escaping from the bulb has to bubble through concentrated sulphuric acid, which retains all moisture. The gas passes up the central narrow tube (*b*) and then down again in the way shown by the arrows. The shaded portion is that occupied by the sulphuric acid. The upper part of the neck (*a*), in the neighbourhood of the perforated stopper, having been slightly greased by a feather, the neck is charged with moderately dilute sulphuric acid, and the stopper, which must be quite dry, inserted. The tap (*e*) is, of course, previously closed, and the desiccating tube is charged with pure concentrated sulphuric acid. The apparatus must be wiped until quite dry outside and then weighed. About a gramme of the sample is then placed in the flask by means of the stoppered tubule (*c*), and the flask again weighed, the increase being the exact weight of the ore. A piece of narrow caoutchouc tube is next slipped over the perforated stopper of the desiccating neck, the stopcock (*e*) opened, and nearly the whole of the dilute acid sucked into the bulb. The stopcock is then closed and the suction discontinued. The acid acts upon the ore, generating carbonic acid, which bubbles through the strong sulphuric acid. After a time, when the current slackens, the bottom of the bulb is cautiously heated over a steam bath and the apparatus gently shaken. When no further evolution of gas can be promoted in this way, the stopcock is again opened and a current of air drawn through the bulb by sucking through the caoutchouc tube. After all carbonic acid has in this way been removed from the interior of the apparatus, the bulb is wiped quite dry and the whole allowed to cool. The weight is now less than it was after the addition of the ore, and the difference is the amount of gas that has been given off. The result is simply calculated to percentage of carbonic anhydride (CO_2).

Before estimating carbonic acid in this way the analyst may test for its presence by adding dilute acid to a portion of the powdered ore. Ores containing carbonates effervesce owing to the escape of carbonic anhydride gas, which, when passed through clear lime water, turns the liquid milky. Slags do not contain carbonic acid.

CHAPTER XIV.

THE DETERMINATION OF SILICIC, TITANIC, AND PHOSPHORIC ACIDS, AND SULPHUR.

Boiling with aqua-regia cannot be depended upon to decompose an ore or slag and yield a residue of silica; very frequently when the substance is apparently decomposed a white residue containing alumina remains. This, for which the term "siliceous matter" is appropriate, can be decomposed by fusion with alkaline carbonate or by treatment with hydrofluoric and sulphuric acids. But the most satisfactory way of estimating silica in an insoluble sample, or when there is any doubt as to the nature of the residue, is to fuse the ore directly with sodium carbonate. Ten grammes of the finely-powdered sample are mixed with 50 grammes of pure sodium carbonate and a little pure nitre and fused for half-an-hour in a capacious platinum crucible. The fusion is extracted with hydrochloric acid in a porcelain dish, and the solution evaporated to dryness. The residue, which contains sodium chloride, free silica, and basic chloride of iron, is re-moistened with concentrated hydrochloric acid, and taken a second time nearly to dryness. The dry residue is now treated with hydrochloric acid until everything except the silica dissolves, the sodium chloride, which is rather insoluble in the strong acid, going readily on addition of water. The silica is filtered off and the filtrate is diluted to a litre, and preserved for the estimation of the bases, phosphoric acid, etc. The silica from ten grammes of sample is sometimes a considerable quantity, weighing 3 or 4 grammes, but if care be taken in igniting the precipitate the accuracy of the analysis is increased, rather than otherwise, by the weight of the silica.

The silica, after ignition and weighing, is mixed with pure sulphuric acid and evaporated several times with pure hydrofluoric acid which has been made in an apparatus of platinum. If a residue remains titanic acid is probably present. The weight of the ignited residue must be substracted from the total silica, and the residue preserved for further examina-

tion. If titanic acid is present in the ore, part of it will be found with the silica, and part with the iron and alumina, in the precipitate produced by ammonium acetate and acetic acid.

The bases are determined in part of the solution filtered from the silica and made up to a litre as described previously. For the determination of phosphoric acid 500 cubic centimetres of this solution, representing 5 grammes of the sample, are diluted somewhat, nearly neutralised by ammonia and boiled. The boiling liquid is treated with very dilute ammonia until the colour deepens considerably, and the iron and alumina are then precipitated with ammonium acetate and acetic acid. The precipate is redissolved in dilute hydrochloric acid and the precipitation with ammonium acetate repeated, as described in the chapter on the determination of manganese in steel. The two filtrates are mixed and preserved for the determination of manganese. The precipitate, which contains the iron and alumina and the whole of the phosphoric acid (and part of the titanic acid), is redissolved in hydrochloric acid and the iron reduced with sodium sulphite. The solution is neutralised with ammonia and precipitated with ammonium acetate in the usual manner, only as much iron must be allowed to remain in the ferric condition as suffices to give the precipitate a pink tint, but this much is necessary.

The precipitate is now dissolved and treated in the way described in the chapter on "The Determination of Phosphorus by Magnesia." The hydrochloric acid solution is mixed with citric acid and then with ammonia and magnesia mixture. After standing all night the ammonium magnesium phosphate is filtered off, washed with dilute ammonia, ignited, and weighed as magnesium pyrophosphate (and afterwards tested for arsenic). The iron in the filtrate is precipitated with ammonium sulphide, the precipitate filtered off, the filtrate evaporated to dryness, and the residue ignited to destroy the organic matter. This ignited residue and the residue obtained by evaporating the silica with sulphuric and hydrofluoric acids are now mixed and fused with potassium bisulphate. The fusion is treated with cold water and filtered from any slight residue; the clear dilute liquid is then boiled for some

hours, the evaporated water being supplied from time to time, and afterwards allowed to stand over night. In order to avoid bumping, a current of carbon dioxide may be passed through the liquid during the ebullition. The solution must be dilute and the greater part of the free acid neutralised by ammonia. The titanic acid is precipitated by the boiling and is filtered off, washed with dilute sulphuric acid, ignited with a little ammonium sulphate, and weighed as titanic anhydride (acid) (TiO_2). As titanic acid is slightly hygroscopic it should be weighed as quickly as possible. After filtering off titanic acid the filtrate is neutralised still further with ammonia and again boiled to see whether any more titanic acid is precipitated.

In ordinary cases titanic acid is absent and the estimation of phosphorus can then be made by the molybdic acid method if preferred. The solution of the basic acetate precipitate in hydrochloric acid is once or twice evaporated with nitric acid to eliminate hydrochloric and acetic acids, and the molybdic acid reagent employed in the manner described in the chapter on "The Determination of Phosphorus by Molybdic Acid." The weight of the yellow precipitate multiplied by ·0372 gives the amount of phosphoric anhydride (acid) (P_2O_5) in 5 grammes of the sample.

THE DETERMINATION OF SULPHUR.

The determination of sulphur in an ore or slag may be made in a separate portion of the sample, or the remainder of the solution from the silica or siliceous matter may be used. In the former case the sample is treated with aqua regia, free from sulphur, as described in the chapter "On the Determination of Sulphur." The solution is evaporated as there described, and the siliceous matter is filtered off.

The filtrate must not occupy a large volume, and the excess of free acid must be reduced to a minimum by evaporation until a crust begins to appear on the surface. Water and, if necessary, a drop of hydrochloric acid are then added, and the resulting solution contains a minimum of hydrochloric acid. The details of the subsequent precipitation as barium sulphate should be conducted as described in Chapter V. It is evident that if barium is contained in an ore special precautions must be adopted in the search for sulphur. The sulphur in presence of barium remains as

sulphate mixed with the silica, and may be separated from the barium by fusion with alkaline carbonate and treatment of the fusion with water. The barium remains behind as carbonate and the sulphur dissolves as sodium sulphate. The silica also dissolves as sodium silicate and must be separated by treatment with hydrochloric acid before the sulphur is precipitated.

CHAPTER XV.

THE DETERMINATION OF THE BASES.

The mixed filtrates, after twice precipitating the iron and alumina with ammonium acetate, contain the manganese, zinc, lime, and magnesia. For the estimation of manganese the liquid, after concentration and thorough cooling, is mixed with bromine until it is dark brown, and then with excess of ammonia; the manganese is precipitated as hydrated peroxide on boiling. The details of the precipitation have been described in a former chapter. The precipitate is separated by filtration, washed, ignited, and weighed as Mn_3O_4. It is next dissolved in sulphuric acid and a crystal of oxalic acid, and the manganese sulphate gently ignited and weighed in platinum. The manganese sulphate may contain small quantities of calcium (barium, zinc, etc.), sulphate, which must be separated. The ignited mixed sulphates are treated in the crucible with a small quantity of water, containing a drop of sulphuric acid, which dissolves the manganese sulphate, and the solution is then diluted with enough strong alcohol to make the mixture proof spirit, in which the calcium and barium sulphates are insoluble. The residue is washed with alcohol on a small filter, ignited and weighed, and the weight subtracted from the original manganese sulphate. The ammoniacal filtrate from the hydrated peroxide of manganese, which contains the remainder of the lime and the magnesia, is concentrated by evaporation to a small bulk after addition of hydrochloric acid, which forms ammonium chloride. The liquid is mixed with some ammonia and ammonium oxalate and digested at a gentle heat for a few hours. Calcium oxalate falls as a heavy crystalline precipitate, which is filtered off and washed. A little sulphuric acid is dropped into the apex of the filter, which is folded up and placed in a platinum crucible. The sulphuric acid converts the oxalate of calcium into sulphate, but to ensure complete conversion the precipitate, after combustion of the filter paper, is again treated with sulphuric

acid. The weight of this precipitate, added to the weight of the calcium sulphate, left after lixiviation of the manganese sulphate with water and alcohol, multiplied by ·4118, gives the total lime (CaO) in five grammes of the sample. To the filtrate from the calcium oxalate, which contains the magnesia, ammonia and a solution of hydric disodic phosphate are added, and the liquid is stirred with a glass rod. The magnesia comes down as crystalline ammonium magnesium phosphate, which must be washed with ammonia, and converted into magnesium pyrophosphate by ignition, the operation being the converse of the estimation of phosphoric acid by magnesia mixture. The weight of the precipitate multiplied by ·3604 gives the weight of magnesia (MgO) in five grammes of the sample.

For the determination of the alumina and oxide of iron one hundred cubic centimetres of the original solution, corresponding to one gramme of the sample, are precipitated by ammonium acetate, the precipitate redissolved in nitric acid and reprecipitated by ammonia. The hydrated alumina and oxide of iron are washed with hot water until the wash water is free from chlorine, and then ignited and weighed. The precipitate is next dissolved in acid, or by fusion with bisulphate of potassium, and the iron reduced by zinc and titrated with standard bichromate. The quantity of ferric oxide (Fe_2O_3) corresponding to the iron found in this way, and the quantity of P_2O_5 calculated from the result obtained from the determination of phosphoric acid, are subtracted from the total weight of the precipitate thrown down by ammonia. The remainder is alumina, and perhaps a trace of silica and titanic acid. If the total iron has been previously determined, as described in chapter XI., the titration of the precipitate obtained by ammonia is of course unnecessary, but it may be used to confirm the former determination.

The determination of the alkalies is most conveniently effected by the use of pure hydrofluoric acid. One or two grammes of the sample in a state of very fine powder are made into a paste with pure concentrated sulphuric acid on the bottom of a platinum dish. To the pasty mass hydrofluoric acid prepared by distillation from platinum is added, and the liquid evaporated. The treatment with hydrofluoric acid is repeated once or twice until the residue

no longer feels gritty. The greater part of the sulphuric acid is evaporated over the bunsen burner, the residue digested with hydrochloric acid and the solution filtered from any insoluble particles. The clear dilute liquid is then mixed with ammonia until only slightly acid, and a solution of pure barium chloride is employed in the least possible excess to remove the sulphuric acid. The filtrate from the barium sulphate contains the iron and alumina, the lime and magnesia, together with chloride of ammonium and the excess of barium chloride from the previous operation. This solution is mixed with ammonium carbonate and ammonia, and a few drops of ammonium oxalate, whereby the iron and alumina are precipitated as hydrates, carrying down the phosphoric acid, and the calcium and barium are precipitated as carbonates. The filtrate contains the magnesia and alkalies, and must be evaporated to dryness and ignited to expel ammonia salts. The residue when treated with a little water dissolves with the exception of a portion of the magnesia; pure precipitated oxide of mercury shaken up with water is then added and the liquid evaporated to dryness in a platinum dish with frequent stirring. The residue is dried and gently ignited to expel chloride and oxide of mercury, and the residual magnesia treated with a small quantity of hot water. The filtrate containing the alkalies as chlorides must be evaporated to dryness and the residue very gently ignited. The function of the oxide of mercury is to cause the decomposition of that portion of the magnesium chloride not decomposed by the first evaporation.

The alkaline chlorides are weighed, and then dissolved in a small quantity of water and one or two drops of hydrochloric acid. A slight excess of platinum chloride over that required to form double chloride with the potassium and sodium is then mixed with the solution, and the whole evaporated nearly to dryness on a water bath. The residue is moistened with a small quantity of water, and again taken down nearly to dryness, to expel the excess of hydrochloric acid. A little more platinum chloride solution is then poured upon the precipitate, and the mixture set aside in a cool place and stirred occasionally. The precipitate, after about an hour, is then transferred to a small filter, the basin rinsed with a few drops of platinum

chloride solution, and the precipitate washed with a few drops more. The filter and the precipitate are next washed with the smallest possible quantity of alcohol of 95 per cent., and dried at 100° C. The dried precipitate is transferred to a porcelain crucible, and further dried at 100° C. The filter paper is burnt on the lid, and the weight of the residual platinum and potassium chloride is calculated to potassio-platinic chloride, and added to the weight of the main quantity. The factor ·1927, converts the precipitate to the corresponding amount of potassium oxide (K_2O). The weight of the double chloride multiplied by ·3050, gives the corresponding amount of potassium chloride, and this substracted from the total weight of the alkaline chloride, gives the amount of sodic chloride; this again multiplied by ·5302, gives the corresponding quantity of sodium oxide (Na_2O). Barium sulphate, when employed to convert sulphates into chlorides, carries down notable proportions of alkali, and it is therefore necessary in very accurate analyses to dissolve the precipitate of barium sulphate in strong sulphuric acid, and reprecipitate by addition of water. The solution then contains the alkali as sulphate, which is recovered on evaporation.

Lead acetate may, with advantage, be employed instead of barium chloride, to remove the sulphuric acid. In this case alcohol must be added, to render the lead sulphate insoluble; the lead is best removed from the filtrate by sulphuretted hydrogen. Hydrochloric acid must be added during the final evaporation of the solution after the separation of magnesia.

CHAPTER XVI.

THE ANALYSIS OF FUEL.

THE DETERMINATION OF MOISTURE AND ASH.

The determination of moisture in a sample of coal or coke is made by drying a known weight of the sample at the temperature of boiling water.

A definite weight, about three grammes, of the powdered fuel is spread over the bottom of a dry watch glass or small wide beaker, and placed in the water oven for an hour. In the case of coal it is not advisable to dry longer than this, otherwise the sample begins to gain in weight from absorption of oxygen. The watch glass and contents are left to cool under the desiccator and then weighed, the loss is the moisture. The ash of the sample is determined by ignition in the air. The operation succeeds best in a platinum dish heated in a muffle, but it can be performed over a good Bunsen burner. In order to determine the ash of coke it is necessary to weigh the platinum dish, add 2½ grammes of the sample, and ignite to bright redness in a muffle for half an hour. The carbonaceous matter burns away and leaves an ash, which is red if it contains much iron or reddish white if only a little iron is present. When the ash appears to be quite free from unburnt coke it is cooled and weighed. It is then replaced in the muffle and again ignited for ten minutes. If the second weighing is the same as the first the operation is complete, but if not the ignition must be repeated until constant weighings are obtained. A high temperature and a good current of air facilitate the combustion of the coke. In the case of coal, the same quantity (2·5 grammes) is weighed into the dish, which is then cautiously heated to coke the sample, and the subsequent operations are as described above. Sometimes it is convenient to use the portion of sample on which the moisture was determined for the estimation of ash. The drying is then done in the platinum dish, and the dried quantity is afterwards burnt to an ash.

CHAPTER XVII.

THE DETERMINATION OF SULPHUR.

In the last chapter the method of extracting the ash or incombustible matter in fuel was described, but for many purposes it is also necessary to know the exact percentage of sulphur. If, for instance, coke which is to be used in the blast furnace for the manufacture of pig iron contains a large quantity of sulphur, this enters into the iron and impairs its quality to a very serious extent. The iron smelter has therefore to be very careful to select coke as free as possible from sulphur. It can never be obtained quite free, and this is one reason why English pig iron is never so good as those varieties of iron made in foreign countries where wood is abundant and charcoal cheap. For domestic purposes also it is well to select fuel free from sulphur, as this element, when the coal is burnt, passes off as sulphur dioxide, and after a time condenses in the form of sulphuric acid, which rapidly corrodes paintings, furniture, and other articles found in dwellings. The presence of sulphur in combination with oxygen is one reason why the fogs prevalent in London are so acid, so corrosive, and so unlike the ordinary white mist of the country.

The sulphur in coke may be determined by roasting an intimate mixture of the coke, with three times its weight of pure slaked lime. The carbonaceous matter burns away leaving the sulphur in the residue as calcium sulphate. Three grammes of the coke are a convenient quantity for the purpose.

The mixture is placed in a platinum dish of about three inches diameter, and the surface covered over with a portion of the lime. The dish is then introduced into the muffle, and allowed to remain about half an hour at a good red heat. It is then removed, and the lime stirred up with a wire. The lime is by this time probably quite white. If it is not, the dish is put back into the furnace until no black particles can be found even at the bottom. The dish is next allowed to cool and the lime transferred

without loss to a glass beaker, the last particles being scraped out with a spatula. Hydrochloric acid is then poured into the dish, and thence into the beaker upon the lime, sufficient being used to dissolve the lime when the liquid is afterwards boiled. This can be best effected by standing the beaker upon a hot plate, supported upon an iron tripod stand over the Bunsen burner. When the acid boils the lime dissolves and the sulphur is obtained in solution as calcium sulphate. The liquid is filtered from the insoluble matter, and nearly all the free acid neutralised by ammonia.

The solution is now boiled, a few cubic centimetres of barium chloride added, and the mixture digested at a temperature approaching boiling for an hour. The barium sulphate is thus obtained in a granular form and filters easily. It is collected on a good Swedish filter, and washed about three or four times with hot water; it is then burnt and weighed, and the weight multiplied by ·13734 gives the weight of sulphur. Another method of determining sulphur, which answers for both coal and coke, depends upon the use of oxidising fusion mixture. A mixture of six parts anhydrous sodium carbonate and four parts potassium nitrate, both free from sulphur, is melted in a platinum crucible. The coal or coke is then added in small quantities at a time, care being taken to so regulate the temperature that the action is not too violent. Sometimes pure sodium chloride is mixed with the nitrate and carbonate to render the deflagration less intense. When the whole of the weighed sample is consumed the fusion is dissolved in hydrochloric acid, and insoluble matter separated by filtration. The precipitation with barium chloride is effected at a boiling heat as in the former case, and the subsequent details of the operation are the same.

CHAPTER XVIII.

THE DETERMINATION OF COKE AND VOLATILE MATTER.

It is important in the case of coal to know how it behaves when heated in closed vessels. The value of a sample of coal for gas making depends very much upon the quantity of volatile matter formed when the coal is so treated; anthracite coal, which gives a small proportion of volatile matter, being almost useless for gasmaking, while gas coal, which gives a large quantity of volatile matter, and a relatively small quantity of coke, is the best for this purpose.

Some analytical chemists determine the yield of coke by heating five grammes of the sample in a platinum crucible, with a tightly fitting lid, for three minutes over a Bunsen gas flame, and subsequently for three minutes over a blast lamp.

This method is subject to several disadvantages; the heat is applied much more suddenly than is the case in coking on the large scale, and the air occasionally burns away a little of the coal during the heating. The yield of coke from the same coal varies somewhat according as the heat is slowly or rapidly applied, and the coking of coal on a manufacturing scale is carried out with the complete exclusion of air. The following process of determining coke, due to Mr. Galloway, is superior to the usual one, inasmuch as the conditions of manufacture are retained. In this process the air is completely excluded. The only apparatus required is a furnace, a balance, a large porcelain crucible, a clay crucible, and some pieces of charcoal. The porcelain crucible, which must when half full of coal contain about 25 grammes, is first of all carefully weighed. It is then charged with exactly 25 grammes of the sample in powder. A layer of charcoal powder is then placed upon the bottom of the clay crucible, which must be much larger than the porcelain one, and upon this charcoal the smaller crucible is placed. The space around and above the porcelain crucible is then packed with small pieces of charcoal, from which the dust

has been removed by sifting, and the lid of the clay crucible is finally placed in position. The porcelain crucible is also provided with a tightly fitting lid. The charcoal serves two purposes—it keeps the smaller crucible in position, and what is more important, it prevents the oxygen of the air gaining access to the sample of coal. The clay crucible is next placed in the furnace, well covered up with coke, and kept at a good red heat for an

FIG. 12.

hour. At the expiration of this time it is removed from the fire, and allowed to cool without being disturbed. When it is quite cold the outer lid is taken off, and the charcoal which covers the porcelain crucible carefully removed. The latter is lifted out, adhering fragments detached, and the crucible with its contents is then weighed. The weight thus obtained, less the weight of the crucible, gives the weight of the coke, and as this is yielded by 25 grammes of the sample, it is easy to calculate

the percentage. The volatile matter is obtained "by difference," or, in other words, by the amount lost during the experiment. The porcelain crucible after the experiment is black, but this does not materially affect its weight.

Mr. G. E. Davis classifies coal under the following five heads, according to the amount of coke it is capable of yielding when heated in closed vessels :—

1. Splint coal, burning with a long flame and yielding from 50 to 60 per cent of powdery or slightly-caked coke.
2. Gas coal, or coal of a bituminous nature, burning with a long flame and yielding from 60 to 70 per cent. of fused but deeply-seamed coke.
3. Smithy coal, or true bituminous coal, burning with a long flame and yielding 68 to 75 per cent. of fused compact coke. The coal fuses in burning, leaving the coke in a compact mass.
4. Caking coal, burning with a short flame, leaving from 75 to 82 per cent. of fused compact coke.
5. Anthracite, or smokeless steam coal.

CHAPTER XIX.

THE DETERMINATION OF THE HEATING POWER OF FUEL.

The quantity of heat a sample of fuel can yield when completely burnt in air can be determined in various ways. According to one method the fuel is mixed with excess of lead oxide, the mixture raised to redness, and the button of reduced lead weighed. This method, which was proposed by Berthier, does not yield good results. It is a measure of the reducing power but not of the heating power of the fuel.

Another plan is to burn the fuel in a crucible in a current of air from a bellows, and pass the products of combustion

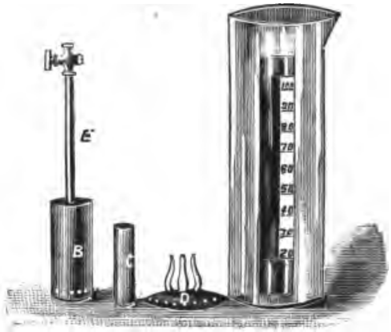

Fig. 13.

through a worm of copper surrounded by a known weight of water. The crucible which forms the firegrate is surrounded by a larger one which serves to retain the heat, and the size and capacity of the apparatus are considerable. The results are good, and represent the result likely to be obtained in actual practice, but, owing to the size and expense of the apparatus and the amount of labour involved, this method, due to Dr. Ure, is seldom or never adopted. In the ordinary course the determination is made by means of the apparatus shown in Fig. 13. This consists of an arrangement for burning a sample of the fuel in a chamber

surrounded by water, by means of solid substances, capable of furnishing the oxygen required for the combustion. The water is contained in the outer glass vessel, which is filled to the mark and then contains 29,010 grains. Thirty grains of the fuel, in a state of fine powder, are weighed out and intimately mixed with from ten to twelve times as much of the oxidising mixture. This is compounded of potassium chlorate three parts and potassium nitrate one part, both being well dried and intimately mixed in fine powder. For cannel or bituminous coal 300 grains of the mixture are sufficient, but for anthracite and coke at least 360 grains are required. The mixture is placed in a stout copper cylinder (*c*), which is open at the top, and fits upon the centre of the stand (*d*). When a free burning fuel is under examination, the cylinder should be of the usual elongated pattern, but for anthracite and coke a shorter, wider cylinder is more suitable. Both forms are supplied with the apparatus. The immediate space surrounding the cylinder (*c*) is enclosed by a wider cylinder (*b*), also of copper, which fits over springs attached to the base (*d*) in such a manner that when (*b*) is lifted up it carries (*d*) with it. A narrow tube (*e*), furnished with a stopcock, establishes a communication between the interior of (*b*) and the air. The mixture having been placed in the cylinder, the tube (*e*). is poked with a wire to make sure that it allows a free passage, and the stopcock is closed. About half an inch of thick cotton thread, previously soaked in a solution of lead nitrate and dried, is then inserted into the top of the mixture in the cylinder. The temperature of the water in the outer glass vessel is then taken by a Fahrenheit thermometer; the water should be as near 60° F. as possible. Immediately after the temperature has been taken a light is applied to the cotton thread, and the cylinder (*b*) is placed in position. The whole system is then lowered as quickly as possible into the water. The cotton thread acts as a slow match, and after an interval which serves for the immersion of the apparatus, the mixture of fuel, chlorate and nitrate is inflamed. Combustion takes place rapidly with abundant evolution of gas, which escapes through the holes at the bottom of (*b*), and rising through the water communicates to it the heat of combustion. As soon as the action is over the stopcock is

opened, when the water rises in the interior of (*b*) and abstracts the heat from the copper. The tap is then opened, and the bell-shaped vessel with the attached foot moved up and down once or twice to mix the liquid, and the temperature is at once taken. The amount of water is such that the number of degrees expressing the increase in the temperature, when increased by one tenth to compensate for the heat absorbed by the copper, gives at once the required heating power of the fuel. The meaning of the figures is this: Suppose the temperature rises 10 degrees F., which, after the addition of one tenth, equal 11 degrees, the fuel represented by the sample is capable, when completely burnt, of boiling off as steam 11 times its own weight of water from water already at the boiling temperature.

CHAPTER XX.

THE ANALYSIS OF GASEOUS FUEL, BLAST FURNACE GASES, ETC.

THE determination of the constituents of furnace gases is readily made by means of an apparatus devised by Mr. Stead. The essential features of the apparatus are shown in the accompanying diagram (Fig. 14). A is a glass tube of half an inch diameter, and its length is divided into 270m.m. The upper portion of this tube is contracted and joined to a horizontal capillary tube which has two stopcocks, G and E. At the upper part of A two platinum wires are hermetically sealed into the glass, and serve for the passage of an electric spark when it is desired to explode mixtures of gases. The lower part of A is also contracted, and is connected to a three-way U tube, the lowest limb of which is in connection with the mercury reservoir C. B, a tube of the same diameter as A, is also connected with the mercury reservoir, but it is in communication with the air at its upper end. D is the "laboratory tube" in which the gas under examination is exposed to the influence of caustic potash, and the stopcock G cuts off or makes communication between this tube and A. The stopcock E opens into the air, and is used to take in and expel the gas. F is a cathetometer connected to the sliding spirit level F^1, and is used to read off the graduations on A. The tubes A and B are surrounded by wider tubes through which is passed a current of water from the main, with the object of keeping the temperature of the gases constant during the continuance of the experiment. The mercury reservoir C slides in a groove between two pulleys, and is counterbalanced by a weight; about three pounds of mercury are required.

The sample of gas is taken by means of the apparatus shown in Fig. 15. This consists of a strong glass cylinder containing mercury. A pipette of about 50 cubic centimetres capacity is placed in the cylinder, the upper tube of the pipette passes through the india-rubber stopper which closes the cylinder, and the lower tube is open for the passage of mercury. To the upper open end

of the pipette a strong india-rubber tube carrying a screw pinch tap is securely fastened. The sample of

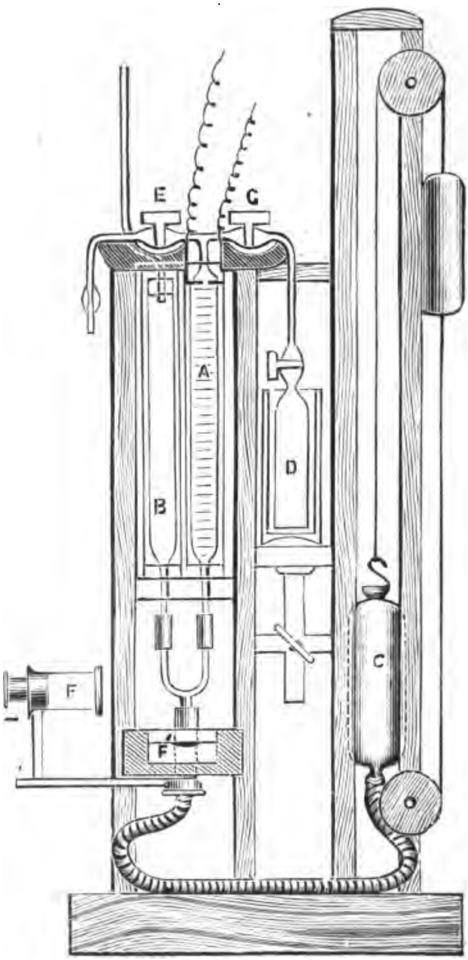

FIG. 14.

gas is obtained from the furnace by means of a tube which is passed through a hole and luted in. The

gas being under pressure inside streams outwards through the tube. The pipette is first filled with mercury to the extremity of the rubber tube, and the pinch tap closed. The rubber tube is then slipped over the tube from which the gas is issuing from the furnace, and the screw tap opened, when the mercury descends and draws gas into the pipette. The screw tap is again closed and the free end of the india-rubber tube filled up with mercury, the last bubble of air being squeezed out. The india-rubber tube is then connected to the gas apparatus, which has been filled with mercury, and the tap E is opened, G having been previously closed. By lowering the mercury reservoir gas is drawn into the measuring tube, and when the required amount has passed in E is closed. The reservoir C is then raised until the mercury is at the same level in

FIG. 15.

the tubes A and B, when the reading of A is made as accurately as possible with the cathetometer. The stop-cock G is now opened and the gas driven over into D, which contains a solution of caustic potash. In a few minutes the carbonic acid is completely absorbed and the gas is returned to the measuring tube A and its volume again read off. The difference between the two readings is the volume of carbonic acid. The gases from the blast furnace are always saturated with water, and hence no correction is necessary for the tension of aqueous vapour. In analysing other gaseous mixtures it is necessary to make sure that the same condition of saturation prevails.

While G is closed and the gas is in the laboratory tube the gas which remains in the capillary tube to the right of C is expelled by raising the mercury reservoir and opening

E. After the gas has been returned from D to A and measured, a supply of oxygen gas is connected to E and a sufficiency drawn into the measuring tube. In order to mix the oxygen with the other gas, and also to ensure complete saturation with aqueous vapour, the contents of A are driven over into the laboratory tube, and after a few minutes brought back again to A, where the volume is again read. An electric spark is then passed through the gas which causes an explosion. After the gas has cooled its volume is again noted, the difference is the contraction due to the chemical action. It is again forced over into the laboratory tube, and the carbonic acid due to the union of carbonic oxide with oxygen is absorbed. The gas is again passed into A, and its volume observed. The calculations are then made from the following data:—

Let A = corrected volume of original gas.
,, B = corrected volume after absorption of CO_2.
,, C = contraction after explosion.
,, D = volume of CO_2 produced by the explosion.

then

$$A - B = CO_2$$
$$D = CO.$$
$$\tfrac{2}{3}(C - \tfrac{1}{2}D) = H.$$
$$A - (CO_2 + CO + H) = N.$$

Several analyses may be made in an hour by means of this apparatus. The barometric pressure usually remains the same during the time consumed by an analysis, and the temperature of water taken direct from the main is sufficiently constant.

The calibration of the measuring tube is effected by weighing successive quantities of water expelled from it. The tube is first filled with mercury, and then pure distilled water is drawn in. The water is then driven out by small portions at a time, and each quantity accurately weighed. The readings on the tube are taken each time, and the corresponding volumes are deduced from the weighings of the water. A table can be constructed, showing the corrected readings of the measuring tube for each millimetre. For the purposes of blast furnace gas analysis, the laboratory tube need only occasionally be detached; but the apparatus may be used to determine other gases than those named above. In this case an arrangement is provided, whereby the laboratory tube can be readily detached from the apparatus, and another absorbent made use of.

A simple and for many purposes sufficiently accurate estimation of the constituents of blast furnaces, and other similar cases, can be made by Orsat's method. The apparatus is shown in Fig. 16. The measurements of the gas are made in the glass cylinder (*a*), which is surrounded by a wider glass cylinder containing water and communicates at its bottom extremity with the aspirator (*b*), containing slightly acidulated water, and at its upper extremity by means of a capillary tube with the absorption vessels (*c*) and (*d*). The first of these contains a solution of caustic potash of 1·35 sp. gr., and the second a mixture of ammo-

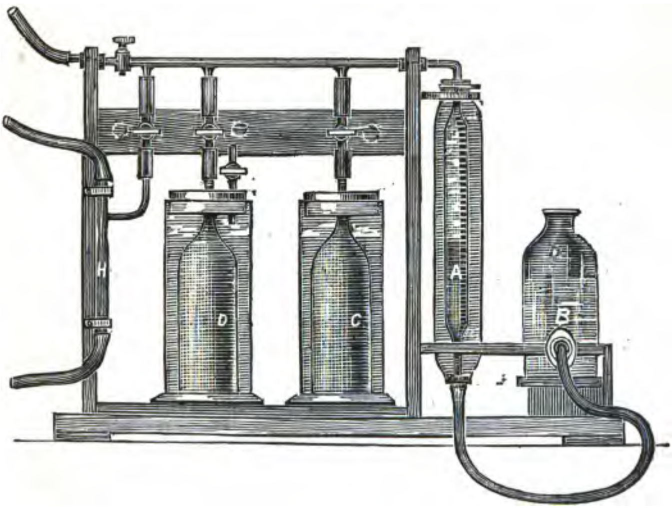

FIG. 16.

nium chloride and ammonia in which a roll of fine copper gauze is immersed. The copper is dissolved, and the resulting liquid has the property of dissolving carbonic oxide (and oxygen).

At the commencement of the experiment the liquids in (*c*) and (*d*) are caused to stand at the marks m and n, their movements being easily controlled by raising or lowering the reservoir (*b*). The sample of gas is taken in by the tube (*b*), and it is advisable to fill the tube (*a*) several times with the gas by raising and lowering the reservoir so as to

wash out the last traces of air. When the surface of the water in (*a*) is at the lower part of the tube at the point marked 100 and the water in the aspirator is at the same level, the stopcock (*g*) is closed. The gas is then forced over into the potash cylinder and allowed to remain a few minutes, it is then returned to *a*, once more forced over into *c*, again returned to *a* and measured. The diminution in volume gives the percentage of carbonic acid. The gas is next forced over into (*d*), where the carbonic oxide (or oxygen) is absorbed, allowed to remain a few minutes, again returned to (*a*) and measured. The diminution in volume gives the amount of carbonic oxide. The whole process can be performed in a few minutes and by comparatively unskilled persons, and the results are satisfactory. The apparatus is provided with a tromp (*h*), which can be used to withdraw the air from the tube connecting the apparatus with the furnace.

TABLE FOR THE ANALYSIS OF IRON ORES.

Dry 20 grammes of the original sample at 100° C. (212° F.) for estimation of MOISTURE; grind the dry ore thus obtained, and reserve for subsequent operations, as follows:—

<table>
<tr>
<td rowspan="2">Estimate CARBONIC ACID in a separate portion.</td>
<td rowspan="2">Estimate "COMBINED WATER" in a separate portion.</td>
<td rowspan="2">Estimate TOTAL IRON and PROTOXIDE OF IRON in separate portions.</td>
<td colspan="3">Fuse 10 grammes with pure sodium carbonate (free from silica and sulphates) and pure nitre. Separate SILICA by evaporation with hydrochloric acid and dilute the filtrate to 1000 c.c. (1 litre).</td>
<td rowspan="2">Estimate ALKALIES in a separate portion.</td>
</tr>
<tr>
<td>Take 500 c.c. (=5 grms.) for estimation of PHOSPHORIC ACID, and estimate MANGANESE, LIME and MAGNESIA in the filtrate from the basic acetate of iron.</td>
<td>Take 400 c.c. (=4 grms.) for estimation of SULPHUR.</td>
<td>Take 100 c.c. (=1 grm.) for estimation of OXIDES OF IRON and ALUMINA.</td>
</tr>
</table>

FACTORS FOR CALCULATIONS.

ARSENIC.

$As_2O_3 \times \cdot7576 = As$
$As_2S_3 \times \cdot4146 = H_2S$

CALCIUM.

$CaSO_4 \times \cdot4118 = CaO$
$CaSO_4 \times \cdot2941 = Ca$
$CaSO_4 \times \cdot7353 = CaCO_3$
$CaSO_4 \times 1\cdot004 = Na_2SO^4$
$CaCO_3 \times \cdot56 = CaO$
$CaCO_3 \times \cdot40 = Ca$
$CaO \times \cdot7143 = Ca$

CARBON.

$CaCO_3 \times \cdot44 = CO_2$
$CO_2 \times \cdot2727 = C$

CHLORINE.

$AgCl \times \cdot24724 = Cl$
$AgCl \times \cdot4077 = NaCl$
$NaCl \times \cdot6068 = Cl$
$Cl \times 1\cdot6479 = NaCl$
$Cl \times 1\cdot338 = MgCl$
$MgCl_2 \times 1\cdot558 = Mg(NO_3)_2$
$MgCl_2 \times 1\cdot2316 = NaCl$

CHROMIUM.

$Cr_2O_3 \times \cdot6862 = Cr$

COPPER.

$\left.\begin{matrix} CuO \\ Cu_2S \end{matrix}\right\} \times \cdot7985 = Cu$

IRON.

$Fe_2O_3 \times \cdot7 = Fe$
$Fe_2O_3 \times \cdot9\ FeO$
$Fe \times 1\cdot286 = FeO$
$Fe \times 1\cdot429 = Fe_2O_3$
$FeO \times \cdot7778 = Fe$

LEAD.

$PbSO_4 \times \cdot6832 = Pb$
$PbCrO_4 \times \cdot6396 = Pb$
$PbCrO_4 \times \cdot73884 = PbS$
$Pb \times 1\cdot1546 = PbS$

MAGNESIUM.

$Mg_2P_2O_7 \times \cdot3604 = MgO$
$Mg_2P_2O_7 \times \cdot2162 = Mg$
$Mg_2P_2O_7 \times 1\cdot0811 = MgSO_4$
$Mg_2P_2O_7 \times \cdot7563 = MgCO_3$
$MgSO_4 \times 1\cdot133 = CaSO_4$
$Mg(NO_3)_2 \times \cdot8378 = NO_3$
$Mg_2P_2O_7 \times \cdot4279 = MgCl_2$
$MgO \times \cdot60 = Mg$
$Mg \times 4\cdot083 = SO_4$

MANGANESE.

$Mn_3O_4 \times 1.1397 = MnO_2$
$Mn_3O_4 \times \cdot9301 = MnO$
$Mn_3O_4 \times \cdot7205 = Mn$
$MnSO_4 \times \cdot3642 = Mn$
$MnSO_4 \times \quad = MnO$

NICKEL (OR COBALT).

$NiO \times \cdot7857 = Ni$
$NiSO_4 \times \cdot37944 = Ni$
$NiSO_4 \times \cdot4829 = NiO$
$Ni \times 1\cdot2726 = NiO$

NITROGEN.

$NH_3 \times \cdot8235 = N$
$NH_3 \times 3\cdot6470 = NO_3$
$NH_3 \times 3\cdot1765 = N_2O_5$
$AgNO_3 \times \cdot7647 = KCN$
$AgNO_3 \times \cdot50 = HCN$
$NO_3 \times 1\cdot371 = NaNO_3$

PHOSPHORUS.

$Mg_2P_2O_7 \times \cdot2793 = P$
$Mg_2P_2O_7 \times \cdot6396 = P_2O_5$
$Mg_2P_2O_7 \times 1\cdot3963 = Ca_3P_2O_8$
Molybdate precipitate $\times \cdot0372 = P_2O_5$
Molybdate precipitate $\times \cdot0163 = P$
$P_2O_5 \times \cdot43662 = P$

POTASSIUM.

$K_2PtCl_6 \times \cdot1603 = K$
$K_2PtCl_6 \times \cdot193 = K_2O$
$K_2PtCl_6 \times \cdot3056 = KCl$
$AgCl \times \cdot52023 = KCl$

SILICON.

$SiO_2 \times \cdot4667 = Si$

SILVER.

$AgCl \times \cdot75276 = Ag$
$Ag \times 1\cdot2121 = AgCl$

SODIUM.

$NaCl \times \cdot3934 = Na$
$NaCl \times 1\cdot2760 = KCl$
$AgCl \times \cdot40743 = NaCl$
$BaSO_4 \times \cdot60944 = Na_2SO_4$

SULPHUR.

$BaSO_4 \times \cdot13734 = S$
$BaSO_4 \times \cdot34335 = SO_3$
$BaSO_4 \times \cdot41202 = SO_4$
$BaSO_4 \times \cdot4206 = H_2SO_4$
$BaSO_4 \times \cdot5837 = CaSO_4$
$BaSO_4 \times \cdot2562 = FeS_2$
$BaSO_4 \times \cdot60944 = Na_2SO_4$
$CaSO_4 \times \cdot5882 = SO_3$
$CaSO_4 \times \cdot706 = SO_4$

TIN.

$SnO_2 \times \cdot7867 = Sn$

TITANIUM.

$TiO_2 \times \cdot60 = Ti$

TUNGSTEN.

$WO_3 \times \cdot7931 = W$

ZINC.

$ZnO \times \cdot8026 = Zn$

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